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CHEMICAL AGING STUDIES ON ANB-3066 AND
TP-H1011 PROPELLANTS

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An accelerated aging study performed with ANB-3066 propellant shows that it conforms to the same aging law or model that describes the aging behavior for TP-H1011 propellant. The crosslinking reaction of imine from the curing agent and carboxyl from the polymer is shown to be essentially complete at the end of the cure period. Evidence also shows that the aging reaction may well be a crosslinking across double bonds in the polymer chains. Chemical and mechanical tests performed at periodic intervals after aging at 75°, 95°, 115°, 135°, and 150° F have led to a better

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understanding of the aging process and have made predictions of future behavior possible. Curves showing a 10 year prediction for tensile stress, strain, and modulus have been included.

Two special studies with TP-H1011 propellant have been made to determine the effects of strain and of a second or multistep aging condition on the aging rate. The results indicate that strain levels to 10 percent have no effect on the aging rate of TP-H1011 propellant in up to 48 weeks at temperatures to 150° F. The two step aging study shows that it is a simple procedure to predict the effect of a second step aging at any temperature between 75° and 150° F by determining the equivalent time at the new temperature caused by the first step aging and then following along the new or second temperature aging path for the time at that temperature. Curves have been included showing the exceptionally good agreement between measured and predicted data for propellant aged at 80° F for 8 years followed by an additional 6 months at 75°, 135°, and 150° F.

FOREWORD

This Technical Report was prepared in accordance
with data line item B004 of DD Form 1423 "Contract Data
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This technical report has been reviewed and is approved
for distribution.

Robert A. Biggers
Project Engineer (MKPB)
Air Force Rocket Propulsion Laboratory

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I. INTRODUCTION

A. BACKGROUND

The chemical structural aging study[1] performed with TP-H1011 propellant indicated that a reliable long time prediction of room temperature aging effects can be obtained from a short time aging study using elevated temperature to accelerate the aging changes. The success of this study suggested that the technique may be applicable to other solid propellants where the aging process is the result of chemical reactions occurring during the aging period.

When more than one chemical reaction occurs and when the reaction rates are affected differently by temperature, the Arrhenius rate equation does not apply and the prediction of effects at one temperature from measurements at another temperature can no longer be easily made. Since the chemical reactions occurring during the cure and aging of solid propellants are varied and complex, it becomes necessary to study these reactions individually to understand the curing and aging mechanisms. It is the study of the chemistry of aging with the TP-H1011 propellant that provided the understanding required for interpretation of the observed changes in mechanical properties.

The CTPB polymer used in ANB-3066 propellant is similar to the PBAN polymer used in TP-H1011. The backbone of the polymer chains is basically polymerized butadiene groups. It is recognized that the cure reactions differ greatly for the two propellants. It was shown that the most likely aging reaction for the TP-H1011

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(1) L. H. Layton, "Chemical Structural Aging Effects," AFRPL-TR-73-27, April 1973

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propellant is associated with the sites of unsaturation on the polymer chain. Since the two polymers are similar in this respect, it is reasonable to assume that the same approach will provide the necessary results for aging interpretation of ANB-3066 propellant.

B. OBJECTIVES

The cure reactions for ANB-3066 propellant differ considerably from those for the TP-H1011 propellant. The cure is complicated by the aziridine to oxazoline rearrangement. The presence of a plasticizer can also possibly interfere with the chemical analyses. An understanding of the chemistry of aging is essential to the interpretation of the aging data.

The objectives of this study are: (a) to develop the method of analysis necessary to define the chemistry of aging, and (b) to correlate these results with the changes in mechanical properties resulting from age. From this, a prediction of the mechanical properties at extended time can be made for ANB-3066 propellant, based on the short time results obtained under accelerated aging conditions. This will make accelerated aging by exposure to elevated temperature environments a meaningful approach to extended time predictions for ANB-3066 propellant.

C. SCOPE

Both the chemical reaction and mechanical property characteristics of ANB-3066 propellant were evaluated in this study. An understanding of the chemistry of cure and aging is required to

interpret the mechanical property characteristics observed.

Determinations of mechanical behavior as a function of aging time and temperature produce an aging rate curve for each temperature used. Extension of any of these curves requires some guidelines. Knowledge of what chemical reactions are occurring and the rates of these reactions at each aging condition provides these guidelines and makes the aging predictions more reliable. Aging data from Second Stage Minuteman propellant studies are compared with the long time predictions made in this program.

II. SUMMARY

An accelerated aging study has been performed with ANB-3066 propellant to define its aging characteristics. It has been found that a procedure for separating the binder from the solids of the propellant has made chemical analyses of the binder simpler and more reliable. The cure reaction of an imine curing agent (HX-868) with the carboxy terminated polymer (CTPB) is for all practical purposes complete at the end of cure and further reaction cannot be detected for the time of the one year study. The amount of insoluble binder (gel) continues to increase at all aging periods throughout the period of study. Gel formation is generally considered to result from crosslinking of the polymer chains, indicating continued reaction. No reaction has been definitely isolated and shown to be the cause for the continued crosslinking; however, iodimetric titration of the binder indicates a decrease in the number of double bonds in the polymer. This suggests a chemical reaction forming crosslinks from one chain to another at sites of unsaturation.

Mechanical properties were measured at periodic intervals of time from end of cure to 48 weeks on propellant held at five aging temperature conditions. Tests were performed at three temperatures to obtain a more complete understanding of the aging effects on the properties. The results of tests at 75 and 125°F indicate that changes in mechanical properties with age follow the same aging model found for TP-H1011 propellant, namely the property, p, is a function of log aging time according to the equation $p = k \log t + c$. The relationship of the aging rates for different aging temperatures remains the same for all tests. While this may not have physical significance, it makes data evaluation for determination of the aging rates more reliable since all the data for all tests support each other. Should one particular set of data have more scatter than can easily be treated, some direction can be achieved from the other results.

The results of mechanical property tests performed at 10°F do not behave in the expected manner. In fact, these results do not agree with previously obtained data from another mix of propellant. It is suspected that the results obtained from the 10°F tests of this study are non-standard and do not represent typical behavior of ANB-3066 propellant.

Two special studies using TP-H1011 propellant were made. The first of these was a two step aging study. Propellant aged for eight years in a motor grain was removed for further aging. Samples were placed in ovens at 150 and 135°F and at 75°F for control. Periodic tests were performed on the three sets of samples for 26 weeks. It was found that it is a simple procedure to predict the

effect of a second step aging at any temperature between 75 and 150°F by determining the equivalent time at that temperature caused by the first step aging and then following along the new or second temperature aging path for the time at that temperature. The effect of a third or fourth or multi-step aging path on the mechanical properties can be determined by shifting across in time from one aging rate curve to another, representing the aging temperatures to which the material will be subjected, and then following the aging rate curve for the time at that temperature.

The second special study was designed to evaluate the effect of prestrain, during aging time, on the rate of aging. Samples of TP-H1011 propellant were prestrained to 0, 2.5, 5 and 10 percent strain and aged at 75, 95, 115, 135 and 150°F for one year. Periodically, during this time, samples were removed for test. The test performed was a measure of the amount of insoluble (gel) binder found in the propellant. This determination only measures chemical change irrespective of other physical or mechanical changes that may occur. It was found that strains up to 10 percent have no effect on the chemical aging rate of TP-H1011 propellant as determined by the percent gel formed during aging.

A prediction of the modulus, stress, and strain capability has been made to 10 years at 75°F and compared with data obtained for the same propellant from a Minuteman Second Stage propellant aging study. These data are available for seven years aging time.

III. TECHNICAL APPROACH

Samples of Minuteman Stage III propellant ANB-3066 were
cast and cured in aluminum lined one gallon cartons for the aging
study. The propellant was obtained from a standard production
mix (No. 7135004) that was made for standardization of materials
and is representative of production propellant. The cartons were
cured in a large oven with the temperature controlled to 115^OF
$\pm$ 2^OF for the curing time of 12 days (288 hours). At the end of
cure, the samples were divided and placed in storage at five aging
temperatures of 75, 95, 115, 135, and 150^OF. One carton sample of
the propellant was sampled periodically during the cure period
for chemical reaction studies. Samples of the cured propellant from
each of the aging environments were removed periodically for chemical
analyses and mechanical property evaluations to determine the
effect of the thermal environments on these parameters during the
aging period.

The propellant binder is cured through the reaction of an
imine curing agent with the carboxyl groups on a prepolymer hydro-
carbon chain. While this appears to be a simple reaction, there
is a possibility for side reactions to occur. It is necessary to
determine how far beyond the normal cure time the cure reactions
are occurring and to what extent they contribute to the observed
changes in mechanical properties. Both the carboxyl and imine
concentrations were determined during the cure and aging time at
115^OF to evaluate their contribution to the aging process. In
addition to the cure reactions, it was anticipated that reactions

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could occur at the sites of unsaturation along the polymer chain. The amount and type of unsaturation was determined at periodic intervals during the aging time period by both iodimetric analysis and nuclear magnetic resonance (NMR) spectroscopy.

Mechanical property evaluations have been made at the same age-time intervals as the chemical analyses, making a direct correlation of the data possible. Uniaxial tensile tests were performed at 10, 75, and 125^OF test temperatures and at ambient and 500 psi superimposed hydrostatic pressure. Stress relaxation determinations were made at a constant 2 percent strain and at 10, 75, and 125^OF test temperatures.

Since rocket motors are generally stored with the grain in some degree of thermal load, the effect of strain on the chemistry of aging has been a constant and thorny problem, with no known satisfactory method of attack. Aging reactions that result in changes in the crosslink density of the polymer network also cause changes in the amount of insoluble binder (gel). It was shown with TP-H1011 propellant that a correlation exists between the amount of gel and the mechanical properties. For this pro-pellant, then, a measure of the amount of gel as a function of aging time is also a good measure of the crosslinks in the binder which, in turn, is related to the mechanical properties.

When a sample of propellant is stored in a strained condition, any new crosslinks formed are unstrained and the effect on mechan-ical properties is not readily determinable. The measure of gel quantity determines the change in crosslinks regardless of the

load on the crosslink. It therefore is a means for measuring chemical crosslink changes and for relating this to the aging rate of the strained sample. To be meaningful, a measure of mechanical response relies on all the crosslinks being formed in the same stress condition.

A study was made of the effect of strain on the rate of gel formation by prestraining samples to 0, 2.5, 5.0 and 10 percent elongation and aging these samples at 75, 110, 135 and 150°F. The amount of gel in the binder was determined at periodic intervals of time to 36 weeks. The propellant used was TP-H1011 because aging rate data had already been established and the correlation of gel content with mechanical properties had been made.

The aging rates for TP-H1011 propellant at four aging temperatures were determined in the initial study[1]. These results were obtained with samples maintained at a constant aging temperature throughout the total aging time. The question naturally arises about what happens to the aging rate when a propellant sample is exposed to various temperature environments for varying times. A sample of TP-H1011 propellant was obtained from the grain of an eight year old motor for this study. The motor had only been exposed to temperatures in the range of 80 $\pm$ 20°F during this time. The sample was cut into smaller pieces for storing at the aging conditions of 75, 135, and 150°F. Uniaxial tensile tests were performed at periodic intervals to 26 weeks to determine the aging rate of the propellant held at each storage condition following the original eight year aging (416 weeks) at a nominal 80°F.

(1) L. H. Layton, "Chemical Structural Aging Effects," AFRPL-TR-73-27, April 1973

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IV. RESULTS

A. CHEMICAL ANALYSIS

1. Binder Separation Procedure

The binder in ANB-3066 represents approximately 12 percent of the total material. The remaining solid material interferes with most analytical techniques for assessment of reactions occurring. Coupled with the fact that chemical reactions occur very slowly in stable composite propellant during the aging period, it becomes readily apparent why chemical analyses of cured, solid propellants have been avoided. Many techniques have been modified and improved to circumvent the problem, but none have been completely satisfactory. A procedure has been used in this study for extracting the solids from the binder. This procedure appears to cause no chemical change in the binder due to the extraction process and produces the sol-gel ratio, ammonium perchlorate and aluminum percentages, and a solids free binder for chemical analysis of functional groups. A round robin study of the procedure is being performed to determine its feasibility and reproducibility as a routine laboratory method. The procedure is briefly outlined below:

    a. Prepare approximately 30 grams of propellant shavings using a microtome or miniature block plane. The shavings should not exceed 10 mils thickness.

b. Using 4 to 6 grams of propellant weighed to the
    nearest 0.1 mg, add 50 ml of benzene, shake for
    15 minutes, decant, centrifuge and decant again.
    Repeat with three more benzene treatments.

c. Evaporate the solvent from the sol sample and
    weigh the fraction.

d. Add 50 ml methanol to the solids portion, shake
    for 10 minutes, decant and discard the solution.

e. Add 50 ml methanol and 50 ml concentrated HCl.
    When the reaction with the aluminum has taken
    place, shake for 15 minutes, decant and discard
    the solution.

f. Add 50 ml methanol to the gel sample, shake for
    10 minutes, decant and discard. Repeat the wash
    6 more times.

g. Squeeze as much solvent from the gel as possible,
    air dry for 2 hours and dry overnight at less than
    100 mm pressure.

h. Weigh the amount of gel.

2. Binder Analysis

a. Sol-Gel Analysis

The sol-gel results are presented in Table I for both
the cure period at 115°F and the aging period to 48 weeks at
five temperatures. These data have been plotted for each aging

temperature and presented together in Figure 1. The individual
data points have been removed because the overlap of data from
the various aging conditions makes it difficult to see the trends
when all points are on one curve. The data points are shown for
the cure period where only one temperature (115°F) was used for
cure. It can be seen that soon after the end of cure the reactions
causing additional crosslinks (as shown by percent gel in the
binder) have slowed down considerably. It is also apparent that
some crosslinking reaction is continuing at all aging temperatures
throughout the aging period, including 75°F.

It is necessary to determine the temperature dependence of
the rate of change of gel so that the rate can be determined at
temperatures other than those measured. The Arrhenius equation
indicates that a plot of log of reaction rate versus reciprocal
temperature of reaction should produce a linear relationship
according to the expression $\ln k = \ln A - \frac{B}{RT}$. The results of the
gel formation rate (determined from a curve similar to Figure 1)
are presented in Figure 2 as a function of reciprocal temperature.
The result is linear with a value of the slope, B, equal to 6762.
The physical significance of B is generally considered to be the
activation energy required for the chemical reaction, and a value
of 6.8 Kcal is low for chemical reactions that can be considered.
There are at least two possibilities that can explain these results.
First, two reactions could be occurring in such a fashion that the
difference in their activation energies is the determined value.
Second, and probably more likely, the reaction rates are diffusion
controlled and the resulting activation energy is for the diffusion

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process. This is evident from the rate equation p = k log t + c

or $\frac{dp}{dt} = \frac{k}{t}$ which appears to be an expression for a diffusion process.

b. Carboxyl and Imine Analysis

Analysis for carboxyl on the polymer chains and imine from the curing agent was performed by direct titration in both the sol and the gel fractions from each sample. As the cure reaction proceeds, it is obvious that both the carboxyl and imine groups should disappear and indeed they do. The results are presented in Table II for both the cure and aging periods. It can be seen that, although some carboxyl and imine remain after the end of cure, the amount of continued reaction soon becomes reduced beyond the sensitivity of the analysis to detect it and, for all practical purposes, the reaction has ceased. The data for the cure ⋅ ⋅ aging period at 115°F have been presented graphically in Figure ⋅ these data are presented on a log time plot to compress the long time scale so that any small changes occurring are made more readily apparent.

c. Total Unsaturation in the Binder

The determination of total unsaturation in the polymer was determined by iodimetric titration of the sol and gel fractions extracted from the aged propellant. The results of these analyses are presented in Table III and shown graphically in Figure 4. It is readily apparent that the data scatter is sufficiently large to preclude determination of reaction rates; however, they leave no doubt that double bonds are disappearing with age and disappearing

more rapidly at the elevated temperatures. These data suggest that the change seen in amount of gel is produced by reaction across sites of unsaturation, resulting in additional crosslinks. Further study of this reaction and its mechanism is necessary for an understanding of the aging process; however, the current data are sufficient to show that in the ANB-3066 system, continued crosslinking in the binder and stiffening of the propellant with age are due to a reaction other than the carboxyl-imine cure reaction.

A study of the aging mechanism made at the Allegany Ballistics Laboratory for the Naval Ordnance System Command[2] supports the conclusion that a reaction other than the cure reaction accounts for the changes in properties with age. This study was on CTPB and HTPB propellant systems and indicated that two mechanisms occur. First is an air oxidation on sites of unsaturation, and second is the AP attack on crosslinking networks. The presence of AP inhibits the air oxidation leaving just the AP attack on unsaturation resulting in continued crosslinking of the binder.

d. Molecular Weight of Sol Fraction

During the cure period, the molecular weight of the sol fraction extracted from the binder was determined by gel permeation chromatography. The results shown in Table IV reveal that initially the cure reaction produces larger molecules, without crosslinks,

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[2] Naval Ordnance Systems Command Exploratory Research, ABL Quarterly Progress Report 74, August 1972, p 49.

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by chain extension. The data in Table I indicate that the first appearance of measurable gel occurred between 48 and 64 hours. It is interesting to note that the molecular weight in the sol decreases at the same time. More significantly, the weight average molecular weight, M_W, dropped drastically while the number average changed only slightly. This indicates that the very large molecules became crosslinked and were taken out of the sol fraction to become gel. These reactions continue, causing the sol fraction molecular weight to decrease to a point only slightly greater than the initial value with approximately the same dispersity. It must be pointed out that the molecular weight is only an indication of reaction in the sol fraction. The crosslinked network also continues to react and indeed is probably the binder fraction of interest in aging studies.

3. <u>Carbon-13 NMR Studies of Cured CTPB Binder Systems</u>

Carbon-13 NMR work was conducted using the ANB-3066 propellant binder materials: Butarez CTLII, HX-868, and polybutene plasticizer. Three types of studies were done:

1. Spectra of the uncured materials were run to determine and assign chemical shift values.

2. The cured system both in the form of gumstocks and cured binder actually extracted from propellant were examined for changes occurring during the curing and aging stages to determine any changes with regard to line intensity and position that could have attributed to the aging process.

3. The cured systems mentioned above were examined for changes in relaxation times of the individual

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lines (T_1's) to determine any changes which
might be attributed to something other than the
normal curing process.

The vast majority of the data collected reflect what would
normally be expected, i.e., an increase in crosslink density with
time. The results obtained thus far indicate that this method
cannot distinguish between increases in crosslink density caused by
the normal cure reaction and increases caused by other mechanisms
during the aging process since the end result is the same as far as
the effects on the intensities and relaxation times of the individual
carbon absorptions are concerned. Theoretically speaking, new absorp-
tion lines should appear when crosslinking occurred through the
pendant vinyl groups in polybutadiene. However, the intensity of
these lines when compared to the extremely low intensity of the
lines from a normal crosslink site would be so small as to make them
virtually unobservable.

A full report of the Carbon-13 NMR work is presented in
Appendix A.

B. MECHANICAL PROPERTIES

The mechanical properties of ANB-3066 propellant were measured
at the same aging time intervals as the chemical analyses. Aging
was performed at ambient relative humidity and at 75, 95, 115, 135,
and 150°F. The tests performed were (1) uniaxial tensile tests at
2 in./min at ambient and elevated pressures (500 psi) and at 10, 75,
and 125°F test temperatures; and (2) uniaxial stress relaxation at
2 percent strain and at 10, 75, and 125°F test temperatures. The
results of these tests are presented in Tables V through XIII.

These data were plotted as a function of log time and a curve drawn through the points representing the best least squares fit of the data. The curves for each parameter for the five aging temperatures were then placed on one figure to show the effect of aging time and temperature. The data points were not included in this presentation because the curves are sufficiently close together that an overlap of data points occurs causing a confusion of data. On each set of curves, however, at least one set of data points has been included to show the scatter band around the curve and to show that the curves are representative of the data. Data points for different temperatures are selected and presented on each set of curves in an attempt to show that all aging temperatures are adequately described without the confusion of having all the points on one set of curves or having all the curves presented separately. These results are presented in Figures 5 through 22.

For those tests performed at 75 and 125°F, the data all indicate that the properties change as a linear function of the logarithm of the aging time. The slope of the curve becomes a form of aging rate and describes the propellant aging behavior for the aging temperature used. This rate should remain the same for other mixes of the same propellant. The point at the end of propellant cure where the property is common to all aging temperatures is a function of the curing condition and can vary from mix to mix depending upon the raw materials used or the temperature of cure. While there is no theoretical basis for using this particular data evaluation (or aging model), the consistent pattern

observed between parameters tested at the same and at varied conditions suggests that the model is good. The same data analysis was used with success with TP-H1011 propellant where ten years of room temperature aging data were available for comparison with a prediction made by extrapolation of the room temperature aging rate curve from six months to ten years. The agreement was excellent. The ANB-3066 propellant has been aged for seven years, and a similar comparison has been made. The aging rate curves for stress, strain, and modulus measured at room temperature and 2 inches per minute crosshead speed have been extended to ten years aging time or to the maximum value attained at 150°F aging condition, whichever came first. This extrapolation can be easily accomplished simply by extending the linear curves, however since it is desirable to compare data from another source it is convenient to use the equation $p = k \log t + c$. Not much has been said about the constant c in this equation, but it plays a large role when data comparisons are to be made. It represents the value of the mechanical property under consideration when $t = 1$ week after cast or very near the end of cure. To compare the aging characteristics of the same propellant type having different initial moduli, stresses, or strains, the data are normalized by using the same constant c in the aging equation.

It was necessary to normalize the seven year aging data obtained from the ten-year aging and storage program[3] to make the comparison

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[3] "Ten-Year Aging and Storage Program," Wing VI Minuteman Second Stage Motors and Components, Contract F04701-72-C-0230, Aerojet Solid Propulsion Company Report 0162-06 SAAS-11 (31 October 1972).

seen in Figures 30-32. Although the initial values for the propellants differed slightly, the aging rates are in excellent agreement. A tabulation of the seven year aging data is presented in Table XVIII along with the normalized values used for this comparison. It is apparent that a better fit would be obtained if the initial stress were normalized to 120 psi and the initial modulus to 412 psi with the other data being increased accordingly. The only normalization that can be done, however, is to match the zero time points assuming they are on the curve.

An Arrhenius temperature dependence plot of log aging rate as a function of temperature gives a surprising linear behavior. The curve for the modulus values determined at ambient pressure is presented in Figure 23. The corresponding plot for TP-H1011 propellant was very non-linear. Predictions of aging behavior at temperatures different from those used for aging should be possible. The slope of the curve is 5500. This represents an activation energy of 5.5 Kcal and is near that for hydrogen bonding or Van der Waals forces. Again, it is possible that the reactions affecting the properties are controlled by diffusion mechanisms and the slope represents the energy required to change this process rather than the usual collision frequency and energy of activation of chemical reactions.

The slopes of the curves for each property and for tests performed at 75 and 125°F have been tabulated and are presented in Table XIV. These data can be used with a measured property for any new mix of ANB-3066 propellant of known age to make a prediction of how that property will change with age in the future

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at any predetermined aging temperature between 75° and 125^OF. Care must be taken that the extrapolation does not extend beyond the value of the property measured at 150^OF for the longest time.

Also included in Table XIV are the aging rates normalized to 150^OF aging temperature. These data show the similarity of all the aging rates for all parameters except the relaxation modulus tested at 125^OF. There is currently no theoretical explanation for the similarity of aging rates.

None of the data for tests performed at 10^OF have been presented with the previous evaluation. These results appeared to be anomalous and interpretation of the observed aging effect is not made. It appears however that during the first ten week aging period that the stress, strain and modulus values all decreased. Then the modulus and stress parameters began to increase with age while the strain continued to decrease. This is shown for the stress parameter in Figure 24. It is not understood how the modulus and stress can decrease as a function of aging time for the 10^OF test and increase linearly with log aging time for the 75° and 125^OF test condition. Data from a previous aging study on ANB-3066 propellant[4] tested at 10^OF after aging at 75^OF did not show this same phenomenon. These results are shown in Figure 25 with the current data for comparison. No explanation for the results has been found that satisfactorily explains the

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(4) S. J. Bennett, "Carton/Motor Sample Correlation,"
      AFRPL-TR-73-83, December 1973

observation. It appears that the plasticizer is becoming more effective at the low test temperature and having no effect at the higher test temperatures. The strain parameter for this test condition follows the log age time law as do all parameters tested at 10°F under superimposed hydrostatic pressure.

C. SPECIAL STUDIES

Two studies were performed using TP-H1011 propellant. The first of these was the two step aging study. Propellant was cut from the grain of an eight year old Minuteman First Stage motor and samples placed in storage at 75, 135, and 150°F to determine the aging rates for the previously aged propellant. The second study was a prestrain aging study. Freshly mixed and cured propellant samples were placed in storage at five aging temperatures (75, 95, 115, 135, and 150°F) at strain conditions of 0, 2.5, 5, and 10 percent to determine the effect of strain on the aging rates.

1. Two Step Aging Study

The propellant sample cut from a motor grain was cut into convenient sample sizes for storage and was wrapped in aluminum foil and placed in the conditioning chambers. During its eight year life, the motor had been maintained at $80 \pm 20°F$ which was assumed to be a constant 80°F storage. One sample was tested on the material as received to determine both the percent gel and the uniaxial tensile properties before further aging. The remainder was tested at 4, 10, and 26 week intervals at the storage conditions of 75, 135, and 150°F. All of these data are presented in Tables XV (percent gel) and XVI (mechanical properties) and in Figures 26, 27, and 28.

It is necessary to have aging rate curves for the single
aging conditions to evaluate these data. These curves are avail-
able from the TP-H1011 aging study [1] and were used by cal-
culating the equivalent 80°F aging rate and using the 135 and 150°F
aging rates as previously determined. The curves in Figure 26
were obtained from a measure of the percent gel in TP-H1011 pro-
pellant binder for aging conditions at 75, 110, 135, and 150°F
for one year. The curves were extrapolated to eight years for
this study. Since the propellant was aged in the motor grain for
8 years at 80°F, the percent gel should be the same as that pre-
dicted by the 80°F curve at 8 years. The same percent gel can be
obtained by aging at higher temperatures for less time. The time
required to do this is determined by following a constant gel line
along a decreasing time path until it intersects the desired aging
rate curve. This indicates that approximately two weeks at 150°F
and five weeks at 135°F would produce the same amount of gel. Now
the second step aging proceeded for 26 weeks and should follow the
same aging rate curve as previously observed for any particular
aging temperature. The solid portion of the curves (Figure 26)
represents this 26 week second step aging process and the points
are the measured amount of gel observed after the second step aging
period. The agreement is exceptionally good. This indicates that the
effect of a multi-temperature aging path on the amount of gel formed
can be evaluated if the aging rate curves have been established for
the propellant of interest.

Since it is obvious that the relationship of percent gel
to mechanical properties is non-linear with the aging temperature at

which the gel is formed, it is of interest to determine the two step aging effect on the mechanical properties. Figures 27 and 28 show the modulus and maximum stress parameters as a function of aging time and temperature. The aging rate curves were again taken from the prior TP-H1011 aging study and were extrapolated from one year to eight years. The time to achieve the same property at elevated temperatures was determined by following a constant property along a decreasing time path to the point of intersection. The 26 week second step aging is represented by the solid portion of the curve and the points represent the data obtained from the second step aging samples. While the data are more scattered than the gel data previously discussed, it is apparent that a very close agreement exists. This indicates that the procedure can be used to predict the long time aging properties of a propellant subjected to a multi-temperature aging path.

The curve for the strain parameter is not shown because the data scatter is sufficient to be confusing. This is particularly apparent with only three aging periods from which to fit the results.

While no data were obtained for the second step aging at $110^{\circ}F$, the aging rate curve was previously obtained. It is a simple procedure, then, to predict the effect of a second step aging at $110^{\circ}F$ by following that curve from the first step aging property level along the aging rate curve for 26 weeks or, for that matter, any desired time. A third and fourth or multi-step aging path can be determined by shifting across in time from one aging rate curve to another representing the aging temperatures to which

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the material will be subjected. The curve is then followed for whatever time that temperature is experienced.

2. Prestrain Aging Study

It is well known that chemical changes occur more rapidly in most rubbery materials as the strain level is increased. There has always been concern that the same phenomenon occurs with solid propellants. Strain is induced in a solid propellant motor grain due to cooldown from the curing temperature to the storage temperature. The effect of this strain on the rate of chemical aging has not been determined. It is a difficult determination to make because the method for assessment of measured results is not clearly understood. First, if the chemical change with age results in any new crosslinks, they are formed in an unstrained condition and become strained when the sample is allowed to go back to its unstrained condition for testing. What now is really zero strain? Second, how long does it take for the sample to relax back to zero strain? Third, if dewetting occurs, how can this effect be separated from a chemical change? Because of these and other problems, the measure of the effect of strain level on the chemistry of aging has not been satisfactorily accomplished.

It seems likely that the change in amount of gel in the propellant binder is a function of the crosslinks in the binder. The number of crosslinks should be a function of the aging chemistry and independent of the rate of relaxation or the dewetting that occurs. A measure of percent gel as a function of aging time, temperature, and strain level should indicate what effect strain

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has on the chemical aging rate at the temperatures used.

Samples of freshly mixed and cured TP-H1011 propellant were cut into specimens three inches long with a 1 in. x 1 in. cross section. End tabs were bonded to these specimens and they were placed in fixtures to strain them to 2.5, 5.0, and 10 percent strain levels. Sufficient specimens were strained to allow testing at 1, 2, 3, 4, 6, 8, 10, 16, 26, 36, and 48 week intervals after aging at 75, 95, 115, 135, and 150°F. Unstrained specimens were also stored and tested at the same intervals for a direct comparison. The only test performed was the analysis for percent gel. The analysis was performed in triplicate. Each section for the individual analyses was cut progressively deeper into the aged sample with no apparent trend from surface to interior. This indicates that surface aging was no different from bulk aging from the standpoint of change in gel content. The results of the analysis are presented in Table XVII and Figure 29.

The isometric representation shows the effect of aging time and temperature as well as strain on the amount of gel formed in the propellant binder. The aging temperature and time effect show an increasing amount of gel as seen before. The interesting result is that the effect of strain on the gel formation rate is insignificant. These important results show that for TP-H1011 propellant strain in the material during aging has no effect on the rate of gel formation. The surface of the sample exhibited no more change in gel content than the interior of the one inch sample. It can be concluded that strains up to 10 percent have no effect on the rate of chemical reactions occurring during aging and therefore no effect on the chemical aging of TP-H1011 propellant.

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V. CONCLUSIONS AND RECOMMENDATIONS

Analyses of propellant binders for extent of chemical reaction
have always presented a problem because of the large amount of
solid material and the interference this material causes with the
analyses. A procedure for separating the binder from the solids
has been used in this study making the chemical analyses feasible.
A round robin study of this procedure is currently being made to
evaluate it as a test procedure. It is recommended that the
results of this round robin be carefully studied as a tool for
propellant property and aging analysis.

Nuclear magnetic resonance (NMR) spectroscopy has been
investigated as a tool to study the aging chemistry in propellant
binders. This study has been made using the latest ^{13}C instru-
mentation at both Thiokol and the University of Utah. While many
interesting chemical effects related to polymer geometries have
been found, no method has yet been devised to utilize the results
in furthering our understanding of aging processes. It is recom-
mended that other means of chemical evaluation of the chemistry
of aging could be more fruitful. For instance, the determination
of total unsaturation in the binder as a function of aging time
and temperature by iodimetric titration has been more useful for
the understanding of aging than the NMR results.

Mechanical properties studies have shown that an empirical
aging law determined to be quite satisfactory for describing the
aging trends for TP-H1011 propellant also applies to the ANB-3066

propellant. No theoretical basis for this aging model exists. It is recommended that study on the aging behavior of these propellants should continue to either give support to the empirical law or define one that is theoretically sound.

The mechanical properties determined on the propellant in this study at $10^{\circ}F$ do not behave in a manner that one would expect. Indeed, other aging data obtained from another mix of the same propellant measured at the same test temperature indicate that the propellant behaves quite normally. The anomalous results obtained in this study are not typical. It is recommended that effort to understand the low temperature test results be made by studying at least one more mix of propellant.

Using the aging law described in this report for ANB-3066 propellant, it is a simple task to extrapolate to long time propellant mechanical properties. This has been done to a maximum of 10 years. Data from an earlier aging study[3] has been plotted on these curves out to the maximum of 7 years available. The agreement between the extrapolated (or predicted properties) curves and the measured data is exceptionally good. These comparisons are shown in Figures 30-32.

The two step aging study indicates that the aging curves can be used to determine the effect of a multi-temperature aging path on the mechanical properties of propellant. The study made was very limited having only three aging periods to show the trends. It is recommended that this study should be extended because of its great value in making predictions of propellant properties from multi-temperature aging studies possible.

A study of the effect of strain level in the propellant sample during aging on the rate of aging showed rather conclusively that strains up to 10 percent had no effect on the chemical aging rate of TP-H1011 propellant. It is recommended that a similar study be made for other propellants to define the effect of strain on the rate of aging.

A summary of the recommendations is listed below:

1. The results of a round robin evaluation of the propellant binder separation procedure should be carefully studied and any suggested improvements in technique be incorporated and the procedure utilized as a tool for propellant property and aging analyses.

2. NMR spectroscopy has been extensively evaluated as a tool for analysis of the chemistry of aging in propellant. It is recommended that in view of the limited usefulness of the results, other methods should be studied to determine the chemistry of aging in propellants. Perhaps iodimetric titration for unsaturation in the polymer can be sufficiently improved to define reaction rates.

3. The aging model used in these studies has been determined empirically and lacks theoretical foundation. It is recommended that means should be sought for either verifying or modifying the aging model to be theoretically sound.

4. Low temperature mechanical property tests (10°F) indicate a non-typical behavior for the propellant in this study. The reason for the behavior is not understood. Studies should continue to determine the cause for the observed behavior to avoid its occurrence in a random fashion in production motor grains.

5. Comparison of the ten year predicted properties for ANB-3066 should be made with results from the OOAMA surveillance program as they become available.

6. The two step aging study indicates that multi-temperature aging can be treated to give a mechanical property prediction regardless of the sequence of the aging path. This needs further study and verification.

7. Strain on the sample during aging appears to have no effect on the rate of aging of TP-H1011 propellant. A similar study should be made for other propellants. The surface of ANB-3066 propellant appears to be particularly susceptible to changes in properties for cut test specimens but the surface in a motor only slightly differs from the bulk of the grain. This technique holds promise to explain this phenomenon.

VI. REFERENCES

(1) L. H. Layton, "Chemical Structural Aging Effects,"AFRPL-
     TR-73-27, April 1973.

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     Quarterly Progress Report 74, August 1972, p 49.

(3) "Ten Year Aging and Storage Program," Wing VI Minuteman
     Second Stage Components Contract F04701-72-C-0230, Aerojet
     Solid Propulsion Company Report 0162-06 SAAS-11, 31 October 1972.

(4) S. J. Bennett, "Carton/Motor Sample Correlation," AFRPL-
     TR-73-83, December 1973.

TABLE I

WEIGHT PERCENT SOL AND GEL
DURING CURE AND AGING OF ANB-3066 PROPELLANT
BENZENE EXTRACTION
MIX 7135004

Storage Conditions

Temp (°F)	Time (wks)	Sol %	Gel %	Total %	Recovery* %
75	4	6.57	5.00	11.57	98.0
	6	6.38	5.11	11.49	97.3
	8	6.06	5.45	11.51	97.5
	10	6.20	5.37	11.57	98.0
	16	6.22	5.51	11.73	99.0
	26	5.79	5.39	11.18	94.7
	36	6.18	5.40	11.58	98.1
	48	5.76	5.61	11.37	96.3
95	4	6.37	5.13	11.50	97.4
	6	6.47	5.12	11.59	98.1
	8	5.88	5.57	11.45	96.9
	10	5.70	5.64	11.34	96.0
	16	6.00	5.42	11.42	96.7
	26	5.97	5.54	11.51	97.5
	36	5.73	5.61	11.34	96.0
	48	5.41	5.85	11.26	95.3

*Based on 11.81% binder target for the propellant.

TABLE I
(continued)
WEIGHT PERCENT SOL AND GEL
DURING CURE AND AGING OF ANB-3066 PROPELLANT
BENZENE EXTRACTION
MIX 7135004

Storage Conditions

Temp (°F)	Time Hour	Time Week	Sol %	Gel %	Total %	Recovery %
115	0	0	11.53	0.00	11.53	97.6
	2	0.0119	11.74	0.00	11.74	99.4
	4	0.0238	11.74	0.00	11.74	99.4
	8	0.0476	11.60	0.00	11.60	98.2
	16	0.0952	11.73	0.00	11.73	99.3
	32	0.190	11.55	0.00	11.55	97.8
	48	0.286	11.76	0.00	11.76	99.6
	64	0.381	9.57	2.00	11.57	98.0
	98	0.583	8.16	3.71	11.87	100.5
	128	0.762	7.33	4.26	11.59	98.1
	177	1.054	6.80	4.74	11.54	97.7
	224	1.333	6.64	4.93	11.57	98.0
	256	1.524	6.49	5.06	11.55	97.6
	340	2.024	6.31	5.19	11.50	97.4
	413	2.458	6.17	5.31	11.48	97.2
		4	6.32	5.11	11.43	96.8
		6	6.31	5.23	11.54	97.7
		8	5.62	5.72	11.34	96.0
		10	5.85	5.61	11.46	97.0
		16	6.08	5.46	11.54	97.7
		26	5.79	5.66	11.45	97.0
		36	5.62	5.76	11.38	96.4
		48	5.63	5.62	11.25	95.2

TABLE I
(continued)

WEIGHT PERCENT SOL AND GEL
DURING CURE AND AGING OF ANB-3066 PROPELLANT
BENZENE EXTRACTION
MIX 7135004

Storage Conditions

Temp (^{O}F)	Time (wks)	Sol %	Gel %	Total %	Recovery %
135	4	6.25	5.28	11.53	97.6
	6	6.05	5.34	11.39	96.4
	8	5.79	5.72	11.51	97.5
	10	5.82	5.80	11.62	98.4
	16	5.66	5.76	11.42	96.7
	26	5.54	5.78	11.32	95.9
	36	5.35	5.98	11.33	95.9
	48	5.38	5.83	11.21	94.9
150	4	6.01	5.40	11.41	96.6
	6	5.80	5.62	11.42	96.7
	8	5.79	5.66	11.45	97.0
	10	5.65	5.83	11.48	97.2
	16	5.32	6.01	11.33	95.9
	26	5.51	5.82	11.33	95.9
	36	5.13	6.10	11.23	95.1
	48	5.31	5.81	11.12	94.2

TABLE II

CHANGE IN CARBOXYL AND IMINE CONCENTRATION DURING CURE
AND AGING OF ANB-3066 PROPELLANT
MIX 7135004

Storage Conditions

Temp (°F)	Time (wks)	Carboxyl, eq/100 gm			Imine, eq/100 gm		
		Sol	Gel	Total	Sol	Gel	Total
Initial Material							
75	4	.0112	.0022	.0073	.0044	.0021	.0034
	6	.0107	.0033	.0074	.0038	.0022	.0031
	8	.0108	.0014	.0063	.0031	.0017	.0024
	10	.0111	.0017	.0067	.0036	.0022	.0029
	16	.0115	.0028	.0074	.0034	.0023	.0029
	26	.0122	.0031	.0078	.0028	.0025	.0027
	36	.0123	.0029	.0079	.0034	.0025	.0030
	48	.0133	.0027	.0081	.0025	.0019	.0022
95	4	.0112	.0020	.0071	.0040	.0016	.0029
	6	.0111	.0013	.0068	.0036	.0019	.0028
	8	.0108	.0019	.0065	.0029	.0021	.0025
	10	.0109	.0016	.0063	.0025	.0019	.0022
	16	.0125	.0034	.0082	.0032	.0030	.0031
	26	.0115	.0077	.0097	.0021	.0031	.0026
	36	.0120	.0025	.0073	.0024	.0023	.0024
	48	.0132	.0026	.0077	.0016	.0014	.0015

TABLE II
(continued)

CHANGE IN CARBOXYL AND IMINE CONCENTRATION DURING CURE AND AGING OF ANB-3066 PROPELLANT MIX 7135004

Storage Conditions

Temp (°F)	Time Hour	Time Week	Carboxyl, eq/100 gm Sol	Gel	Total	Imine, eq/100 gm Sol	Gel	Total
115	0	0	.0292		.0292	.0170		.0170
	2	.0119	.0272		.0272	.0161		.0161
	4	.0238	.0269		.0269	.0152		.0152
	8	.0476	.0258		.0258	.0136		.0136
	16	.0952	.0265*		.0265	.0119		.0119
	32	.190	.0271*		.0271	.0094		.0094
	48	.286	.0316*		.0316	.0077		.0077
	64	.381	.0142	.0015	.0120	.0070	.0046	.0066
	98	.583	.0144	.0055	.0116	.0051	.0036	.0046
	128	.762	.0114	.0060	.0094	.0049	.0032	.0043
	177	1.054	.0115	.0022	.0077	.0030	.0021	.0026
	224	1.333	.0106	.0014	.0067	.0029	.0016	.0023
	256	1.524	.0112	.0025	.0074	.0030	.0015	.0023
	340	2.024	.0115	.0050	.0086	.0025	.0024	.0025
	413	2.458	.0108	.0009	.0062	.0028	.0018	.0023
		4	.0114	.0012	.0068	.0034	.0016	.0027
		6	.0106	.0013	.0064	.0031	.0019	.0026
		8	.0105	.0018	.0061	.0021	.0021	.0021
		10	.0105	.0021	.0064	.0027	.0023	.0025
		16	.0115	.0045	.0082	.0029	.0024	.0027
		26	.0110	.0033	.0072	.0017	.0020	.0018
		36	.0107	.0023	.0064	.0021	.0022	.0022
		48	.0128	.0042	.0085	.0015	.0019	.0017

*Incomplete removal of ammonium perchlorate

TABLE II
(continued)

CHANGE IN CARBOXYL AND IMINE CONCENTRATION DURING CURE
AND AGING OF ANB-3066 PROPELLANT
MIX 7135004

Storage Conditions

Temp ($^{\circ}$F)	Time (wks)	Carboxyl, eq/100 gm			Imine, eq/100 gm		
		Sol	Gel	Total	Sol	Gel	Total
135	4	.0124	.0032	.0082	.0030	.0019	.0025
	6	.0102	.0013	.0069	.0030	.0017	.0024
	8	.0102	.0019	.0061	.0024	.0022	.0023
	10	.0103	.0023	.0063	.0023	.0022	.0023
	16	.0105	.0024	.0064	.0022	.0025	.0024
	26	.0112	.0035	.0073	.0015	.0018	.0017
	36	.0103	.0028	.0063	.0020	.0019	.0019
	48	.0103	.0021	.0073	.0013	.0011	.0012
150	4	.0110	.0015	.0065	.0031	.0020	.0026
	6	.0097	.0015	.0057	.0025	.0015	.0020
	8	.0094	.0010	.0052	.0022	.0021	.0021
	10	.0102	.0020	.0060	.0026	.0028	.0027
	16	.0099	.0019	.0057	.0019	.0018	.0018
	26	.0116	.0028	.0071	.0017	.0019	.0018
	36	.0103	.0021	.0058	.0023	.0022	.0022
	48	.0137	.0021	.0076	.0014	.0014	.0014

TABLE III

IODIMETRIC TITRATION FOR UNSATURATION IN ANB-3066 PROPELLANT MIX 7135004

Storage Conditions

Temp (°F)	Time (wks)	Iodine Number, gm I_2/100 gm Binder		
		Sol	Gel	Total
75	4	207	283	250
	6	204	245	227
	8	187	243	216
	10	200	211	206
	16	205	223	215
	26	192	226	210
	36	191	228	211
	48	195	223	209
95	4	211	284	251
	6	209	258	236
	8	199	248	224
	10	197	248	223
	16	200	239	220
	26	185	206	196
	36	186	231	209
	48	189	233	210
115	4	211	254	235
	6	194	272	237
	8	200	231	215
	10	196	236	216
	16	200	213	207
	26	176	190	183
	36	186	201	193
	48	188	189	189
135	4	197	236	218
	6	191	259	227
	8	195	229	212
	10	210	242	226
	16	192	224	208
	26	184	223	203
	36	182	183	182
	48	187	245	215
150	4	198	255	228
	6	191	237	214
	8	202	241	222
	10	200	231	215
	16	186	222	203
	26	188	205	195
	36	179	174	177
	48	189	238	212

TABLE IV

MOLECULAR WEIGHT OF THE BINDER SOL FRACTION DURING CURE
GPC ANALYSIS
MIX 7135004

Curing Time Hours	Number Average Molecular Weight M_n, Gm/mole	Weight Average Molecular Weight M_w, Gm/mole
0	7010	24600
2	7170	26400
4	7110	23300
8	9600	41100
16	9040	41400
32	9280	42800
48	9700	41100
64	9390	46700
98	9300	39300
128	10290	35300
177	6260	29800
224	7450	31200
256	6850	29700
340	7710	27100
413	7200	25700

TABLE V

TENSILE MODULUS DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 IN./MIN CROSSHEAD RATE AND AT AMBIENT PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Modulus (psi) at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	1550	----	----	----	----
	2	1420	1590	1500	1440	1460
	3	1520	1420	1420	1650	1730
	4	1290	1250	1333	1370	1574
	6	1243	1120	1307	1475	1667
	8	1490	1700	1715	1880	2320
	10	1080	980	1200	1540	1810
	16	1280	1530	1480	1683	2353
	26	1535	1918	1928	2381	2472
	36	1636	1961	2267	2680	2733
	40	1770	2415	2400	2570	2460
	48	1610	1660	1720	2100	2140
75	1.7	392	----	----	----	----
	2	458	472	471	500	516
	3	405	418	449	489	500
	4	471	510	508	533	658
	6	487	490	530	641	716
	8	483	566	630	677	889
	10	502	592	648	742	863
	16	520	571	672	867	927
	26	680	786	755	1029	1034
	36	700	815	970	1190	1270
	40	628	843	900	990	1020
	48	730	790	890	1130	1090
125	1.7	295	---	---	---	---
	2	364	351	381	366	390
	3	345	358	390	419	439
	4	366	384	406	392	562
	6	352	362	397	465	503
	8	354	397	424	493	666
	10	376	452	460	540	656
	16	376	436	470	623	704
	26	455	580	580	750	770
	36	500	630	690	970	955
	40	467	660	656	880	933
	48	530	70.?	720	885	925

TABLE VI

MAXIMUM TENSILE STRESS DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 IN./MIN CROSSHEAD RATE AND AT AMBIENT PRESSURE

MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Maximum Stress (psi) at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	181	-	-	-	-
	2	175	174	172	174	176
	3	163	173	178	184	194
	4	169	163	169	180	188
	6	160	161	174	184	197
	8	159	167	166	183	201
	10	157	145	164	192	209
	16	161	201	178	209	249
	26	180	194	205	221	227
	36	188	211	224	239	244
	40	202	223	234	254	249
	48	192	210	220	235	241
75	1.7	94	-	-	-	-
	2	97	99	98	103	103
	3	101	102	105	107	112
	4	102	107	110	117	125
	6	107	108	111	124	137
	8	103	108	113	124	137
	10	107	111	117	127	137
	16	105	116	120	132	143
	26	113	124	130	144	146
	36	123	135	145	156	164
	40	115	132	141	150	153
	48	129	141	151	161	162
125	1.7	78	-	-	-	-
	2	80	80	80	82	85
	3	85	85	89	90	95
	4	85	87	90	94	104
	6	82	86	90	98	106
	8	81	83	89	98	118
	10	87	92	98	106	116
	16	83	90	94	103	115
	26	85	96	102	112	115
	36	94	106	113	124	131
	40	96	108	115	122	121
	48	102	109	116	129	130

TABLE VII

STRAIN AT MAXIMUM TENSILE STRESS DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 IN./MIN CROSSHEAD RATE AND AT AMBIENT PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Percent Strain at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	31	--	--	--	--
	2	32	29	31	32	33
	3	32	25	26	25	28
	4	29	29	26	29	25
	6	25	25	24	24	22
	8	32	30	28	28	26
	10	31	28	26	26	23
	16	30	26	26	22	24
	26	28	23	23	21	21
	36	29	25	25	22	20
	40	26	24	25	24	25
	48	26	23	27	24	25
75	1.7	42	--	--	--	--
	2	31	34	33	33	34
	3	38	36	36	34	33
	4	42	37	38	39	36
	6	35	36	31	30	31
	8	40	35	33	31	26
	10	34	35	33	30	30
	16	35	32	32	29	27
	26	30	30	30	26	29
	36	33	30	29	26	25
	40	32	30	30	27	26
	48	33	30	29	26	26
125	1.7	41	--	--	--	--
	2	39	41	42	42	38
	3	37	37	35	34	34
	4	40	35	34	38	32
	6	38	29	35	33	28
	8	43	38	39	36	31
	10	37	33	30	30	29
	16	39	38	35	26	30
	26	37	34	30	27	26
	36	32	24	27	21	19
	40	37	30	29	24	23
	48	28	30	24	21	19

TABLE VIII

STRAIN AT RUPTURE DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 IN./MIN CROSSHEAD RATE AND AT AMBIENT PRESSURE
MIX 7135004

Test Temp ($^{\circ}$F)	Aging Interval (weeks)	Percent Strain at Storage Temperatures, $^{\circ}$F				
		75	95	115	135	150
10	1.7	49	--	--	--	--
	2	53	49	51	51	53
	3	52	43	46	41	44
	4	52	47	37	47	39
	6	45	40	40	37	33
	8	48	41	42	36	33
	10	44	40	39	37	33
	16	41	41	40	32	34
	26	42	36	33	29	29
	36	42	35	32	28	23
	40	36	34	32	29	34
	48	32	28	31	30	30
75	1.7	53	--	--	--	--
	2	44	50	45	49	47
	33	50	50	48	47	48
	4	60	53	54	50	47
	6	44	48	43	42	38
	8	53	44	40	36	31
	10	48	49	46	40	36
	16	44	44	40	35	31
	26	38	38	36	32	33
	36	39	38	33	29	28
	40	45	38	34	30	28
	48	39	36	32	29	28
125	1.7	51	--	--	--	--
	2	51	52	57	56	49
	3	46	49	45	46	46
	4	53	46	45	48	37
	6	44	31	38	39	30
	8	54	45	49	42	35
	10	44	43	39	36	34
	16	46	46	43	30	34
	26	41	38	31	30	29
	36	36	27	30	23	26
	40	39	33	33	29	24
	48	32	31	28	24	20

TABLE IX

TENSILE MODULUS DATA FOR ANB-3066 PROPELLANT TESTED AT 2 IN./MIN CROSSHEAD RATE AND AT 500 PSI SUPERIMPOSED PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Modulus (psi) at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	1601	--	--	--	--
	2	1834	1960	1815	1722	1692
	3	2153	2014	2194	2416	2225
	4	1632	1691	1879	1990	1949
	6	1712	1839	1856	2181	2293
	8	1793	1876	1914	2018	2293
	10	1816	2380	2185	2638	3060
	16	1800	1970	2238	2688	2562
	26	1460	1870	1680	1980	2170
	36	2860	2590	3250	3420	3480
	40	1304	1780	2142	2300	2480
	48	1857	2050	2437	2780	2560
75	1.7	488	--	--	--	--
	2	469	625	551	609	655
	3	515	532	563	639	639
	4	554	575	634	657	613
	6	587	582	674	805	800
	8	608	735	702	847	982
	10	596	714	784	948	1076
	16	646	769	855	961	1312
	26	630	794	820	1070	1130
	36	700	800	932	1150	1250
	40	712	838	950	1130	1150
	48	724	970	990	1170	1090
125	1.7	345	--	--	--	--
	2	310	358	385	406	410
	3	391	442	438	489	496
	4	417	462	487	496	595
	6	383	420	460	566	583
	8	491	531	550	639	927
	10	430	494	563	723	717
	16	548	618	645	810	858
	26	523	653	672	812	820
	36	714	857	--	--	1390
	40	535	680	694	870	880
	48	560	680	747	971	940

TABLE X

MAXIMUM TENSILE STRESS DATA FOR ANB-3066
PROPELLANT TESTED AT 2 IN./MIN CROSSHEAD
RATE AND AT 500 PSI SUPERIMPOSED PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Maximum Stress (psi) at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	357	---	---	---	---
	2	371	340	366	340	355
	3	368	366	369	370	370
	4	363	370	377	400	398
	6	364	375	375	396	436
	8	355	365	365	406	423
	10	385	402	405	448	456
	16	372	405	420	424	440
	26	365	374	386	404	407
	36	500	420	540	544	566
	40	320	327	380	400	416
	48	388	412	425	447	452
75	1.7	193	---	---	---	---
	2	183	195	208	209	216
	3	193	200	205	215	324
	4	186	197	221	222	217
	6	194	200	203	218	236
	8	213	226	233	252	276
	10	212	225	240	266	283
	16	214	230	237	264	309
	26	202	229	257	286	312
	36	217	249	250	272	295
	40	237	254	266	296	306
	48	231	267	288	314	314
125	1.7	140	---	---	---	---
	2	137	142	144	147	152
	3	141	152	150	156	164
	4	141	153	159	171	166
	6	141	148	158	176	190
	8	169	163	170	188	205
	10	147	160	175	198	211
	16	155	170	179	196	203
	26	155	170	183	200	218
	36	222	185	269	297	307
	40	163	185	194	215	228
	48	165	191	198	227	231

TABLE XI

STRAIN AT MAXIMUM TENSILE STRESS DATA FOR ANB-3066 PROPELLANT TESTED AT 2 IN./MIN CROSSHEAD RATE AND 500 PSI SUPERIMPOSED PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Percent Strain at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	42	--	--	--	--
	2	47	44	41	45	42
	3	44	41	39	39	39
	4	45	41	41	42	38
	6	44	43	39	40	39
	8	45	47	41	37	34
	10	47	40	41	37	37
	16	41	42	38	37	32
	26	37	35	32	29	25
	36	36	32	31	27	23
	40	41	34	32	28	28
	48	34	31	29	27	28
75	1.7	59	--	--	--	--
	2	58	57	55	49	53
	3	59	52	55	53	58
	4	58	52	53	52	48
	6	55	55	51	55	49
	8	61	52	53	48	44
	10	58	53	52	43	43
	16	52	50	50	41	38
	26	51	42	38	34	28
	36	47	40	36	29	28
	40	47	39	36	34	35
	48	44	39	39	33	34
125	1.7	60	--	--	--	--
	2	61	57	58	58	58
	3	56	55	56	51	50
	4	52	51	52	50	46
	6	53	53	50	45	43
	8	56	49	52	45	40
	10	56	51	54	44	40
	16	53	47	43	38	36
	26	48	40	38	32	28
	36	46	41	34	30	27
	40	44	38	37	30	31
	48	46	38	36	29	31

TABLE XII

STRAIN AT RUPTURE DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 IN./MIN CROSSHEAD RATE AND
500 PSI SUPERIMPOSED PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Percent Strain at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	44	--	--	--	--
	2	49	46	42	47	45
	3	46	45	41	42	42
	4	47	46	43	44	39
	6	46	43	41	42	40
	8	46	49	42	38	35
	10	49	42	43	40	38
	16	42	43	39	37	32
	26	41	39	35	31	27
	36	40	34	32	28	24
	40	44	37	33	30	29
	48	36	32	30	29	30
75	1.7	62	--	--	--	--
	2	61	59	59	51	55
	3	62	54	58	55	60
	4	63	53	55	54	53
	6	58	57	53	56	49
	8	63	54	54	49	46
	10	61	55	54	45	44
	16	54	50	54	42	38
	26	57	45	40	36	33
	36	49	42	37	30	29
	40	50	42	40	35	37
	48	47	41	40	36	35
125	1.7	66	--	--	--	--
	2	69	63	62	66	60
	3	59	60	58	56	54
	4	56	56	56	53	50
	6	57	56	53	48	45
	8	59	52	55	47	41
	10	58	55	56	46	41
	16	54	50	44	39	36
	26	52	44	40	34	29
	36	50	43	36	31	28
	40	47	41	39	32	32
	48	49	40	38	31	32

TABLE XIII

RELAXATION MODULUS DATA FOR ANB-3066 PROPELLANT
TESTED AT 2 PERCENT STRAIN
FOR 10,000 SECONDS AT AMBIENT PRESSURE
MIX 7135004

Test Temp (°F)	Aging Interval (weeks)	Relaxation Modulus (psi) at Storage Temperatures, °F				
		75	95	115	135	150
10	1.7	281	---	---	---	---
	2	232	357	310	299	321
	3	271	272	327	317	394
	4	263	228	291	274	365
	6	296	302	2b7	366	422
	8	261	320	443	455	495
	10	265	342	366	499	512
	16	350	335	394	543	544
	26	321	440	468	676	765
	36	420	560	680	830	770
	40	468	609	739	752	680
	48	380	460	640	690	775
75	1.7	160	---	---	---	---
	2	148	187	202	196	189
	3	196	173	202	189	188
	4	164	219	186	206	248
	6	218	217	222	292	348
	8	200	247	269	315	450
	10	205	246	274	330	411
	16	244	291	340	424	461
	26	156	178	285	260	390
	36	290	300	460	470	590
	40	337	330	440	556	554
	48	290	420	490	620	640
125	1.7	168	---	---	---	---
	2	152	188	175	184	198
	3	188	172	198	164	261
	4	173	175	200	199	240
	6	193	190	238	329	380
	8	195	214	259	298	412
	10	237	294	218	328	391
	16	204	230	312	456	449
	26	225	306	280	417	434
	36	260	270	430	530	640
	40	228	342	365	462	536
	48	274	362	388	533	602

TABLE XIV

AGING RATE OF CHANGE
ANB-3066

Test Temp (°F)	Property	Pressure psi	Aging Rate, k					Normalized Aging Rate				
			75	95	115	135	150	75	95	115	135	150
75	Modulus	Ambient	195	270	365	460	560	.35	.48	.65	.82	1.0
	Stress	Ambient	15	21	28	36	44	.34	.48	.64	.82	1.0
	Strain at σm	Ambient	-3.5	-4.5	-6	-7.5	-9	.39	.50	.67	.83	1.0
	Strain at Rup	Ambient	-6	-8	-11	-14	-17	.35	.47	.65	.82	1.0
125	Modulus	Ambient	170	230	300	395	480	.35	.48	.63	.82	1.0
	Stress	Ambient	14	19	25	33	40	.35	.48	.63	.82	1.0
	Strain at σm	Ambient	-5.5	-7.7	-10	-13.1	-15.5	.35	.50	.64	.84	1.0
	Strain at Rup	Ambient	-7.5	-10.5	-13.5	-17	-21	.36	.50	.64	.83	1.0
75	Modulus	500	206	283	375	483	590	.35	.48	.64	.82	1.0
	Stress	500	36	50	68	86	105	.33	.48	.65	.82	1.0
	Strain at σm	500	-8.5	-11.3	-15.3	-19.3	-23.6	.36	.48	.65	.84	1.0
	Strain at Rup	500	-8.0	-11.8	-16.0	-20.0	-24.5	.34	.48	.65	.82	1.0
125	Modulus	500	161	219	295	380	460	.35	.48	.64	.83	1.0
	Stress	500	25	35	47	60	73	.34	.48	.64	.82	1.0
	Strain at σm	500	-9.1	-12.6	-16.6	-21.5	-26.0	.35	.49	.64	.82	1.0
	Strain at Rup	500	-9.8	-13.8	-18	-23.4	-28.5	.35	.48	.64	.82	1.0
75	Relaxation Modulus	Ambient	115	153	210	267	325	.35	.47	.65	.82	1.0
125	Relaxation Modulus	Ambient	60	105	156	238	318	.19	.33	.49	.75	1.0

TABLE XV

PERCENT GEL IN TP-H1011 PROPELLANT BINDER
PROPELLANT FROM MOTOR 9180
(TWO STEP AGING STUDY)

<u>Storage Conditions</u>

Temp (°F)	Time (wks)	Sol %	Gel %
(1st Step)			
80	8 yr	56.2	43.8
(2nd Step)			
75	4	56.3	43.7
135	4	55.7	44.3
150	4	54.2	45.8
75	10	56.5	43.5
135	10	55.5	44.5
150	10	52.6	47.4
75	26	56.2	43.8
135	26	54.6	45.4
150	26	50.5	49.5

TABLE XVI

UNIAXIAL TENSILE TEST RESULTS, TP-H1011
(TWO STEP AGING STUDY)

<u>Storage Conditions</u>

Temp (^{O}F)	Time (wks)	Crosshead Rate in./min	Modulus psi	Maximum Stress psi	Strain at σ_m %	Strain at Rup %
(1st Step)						
80	8 yrs	0.2	804	108	24	28
		2	911	127	31	32
		20	1590	146	35	38
(2nd Step)						
75	4	0.2	925	111	27	28
		2	1075	129	33	37
		20	1720	154	35	40
	10	0.2	808	97	30	32
		2	960	112	34	38
		20	1552	147	41	47
	26	0.2	651	76	22	24
		2	876	113	33	35
		20	1050	147	36	39
135	4	0.2	330	106	28	29
		2	1000	125	34	37
		20	1420	159	30	35
	10	0.2	820	95	28	31
		2	963	114	34	37
		20	1428	150	39	46
	26	0.2	820	102	20	23
		2	989	130	28	33
		20	1444	164	29	31
150	4	0.2	900	110	28	29
		2	1095	131	32	34
		20	1610	156	36	40
	10	0.2	904	102	24	27
		2	1048	120	31	35
		20	1562	162	38	43
	26	0.2	885	97	17	20
		2	1230	148	21	23
		20	1482	187	26	28

TABLE XVII

EFFECT OF STRAIN ON THE RATE OF GEL FORMATION WITH AGE

Storage Conditions

Time (wks)	Temp (°F)	Percent Gel at Strain Levels, %			
		0	2.5	5.0	10.0
–	end of cure	42.3			
2	75				42.7
	95				42.7
	115		43.8	43.7	43.7
	135		44.4	44.6	44.9
	150	43.7	45.7	45.2	45.7
3	75				41.5
	95				42.1
	115		43.1	42.0	42.8
	135		44.7	43.7	43.8
	150	45.4	45.7	45.6	46.0
4	75	43.0			
	95				42.8
	115		44.8	43.9	43.8
	135		45.6	45.7	45.6
	150	46.6	47.5	46.9	47.7
6	75	42.0			42.6
	95				43.9
	115		45.2	44.6	45.4
	135		43.8	45.7	45.6
	150		48.2	48.0	46.3
8	75				42.4
	95				43.9
	115		45.5	45.3	45.3
	135		46.4	45.9	46.0
	150	48.6	48.7	49.1	48.8
10	75	42.9			42.7
	95				44.2
	115		45.7	45.2	45.5
	135		46.8	46.3	46.2
	150		50.1	49.4	49.1
16	75				43.4
	95				44.7
	115		45.7	46.0	45.6
	135		48.1	47.7	48.3
	150	49.0	51.0	50.7	51.2

TABLE XVII
(continued)

EFFECT OF STRAIN ON THE RATE OF GEL FORMATION WITH AGE

Storage Conditions

Time (wks)	Temp (°F)	Percent Gel at Strain Levels, %			
		0	2.5	5.0	10.0
26	75				43.2
	95				45.5
	115		47.1	47.1	46.7
	135		49.4	49.5	49.5
	150	53.4	53.4	53.1	52.5
36	75				42.4
	95				44.6
	115		47.3	48.1	
	135		49.8	50.1	50.3
	150		53.6	53.6	53.7
48	75	42.9			43.0
	95				45.0
	115		48.5	47.9	48.4
	135		50.4	51.0	50.3
	150		55.1	55.4	55.3

TABLE XVIII

UNIAXIAL TENSILE TEST DATA FROM TEN-YEAR AGING AND STORAGE PROGRAM[3]
Tested at 2 inches/min and 77°F

Storage Temp (°F)	Storage Time (wks)	Measured Property			Normalized Property		
		σ_m psi	ϵ_m %	E psi	σ_m psi	ϵ_m %	E psi
80	1	80	32	392	100	36	392
	26	97	32	489	117	36	489
	52	101	24	729	121	28	729
	78	111	25	782	131	29	782
	120	94	28	562	114	32	562
	130	109	27	749	129	31	749
	156	107	26	771	127	30	771
	182	107	25	725	127	29	725
	208	111	25	883	131	29	883
	232	102	24	828	122	28	828
	256	105	27	771	125	31	771
	312	104	23	739	124	27	739
	364	107	25	750	127	29	750
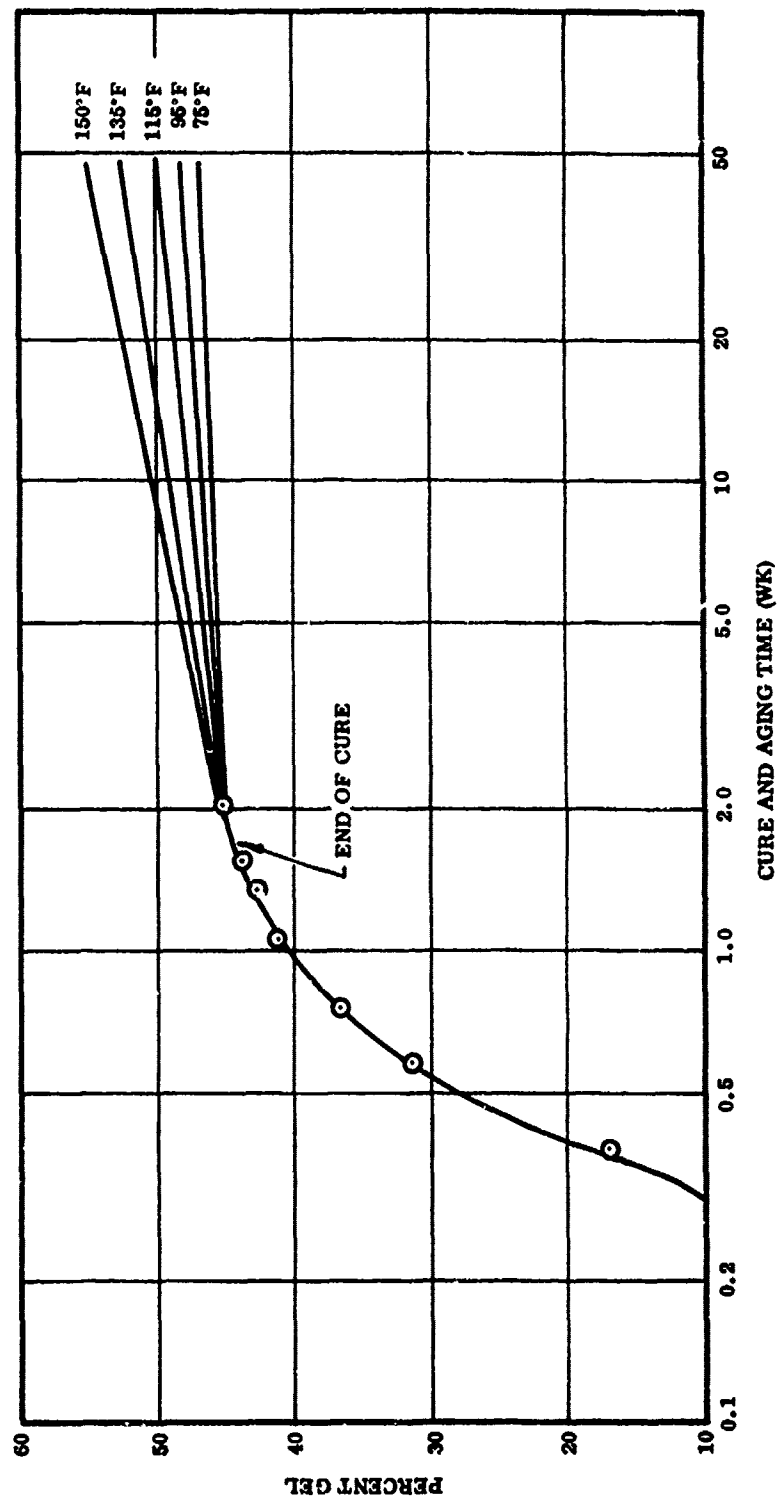
Figure 1. Percent Gel in Propellant Binder, ANB-3066
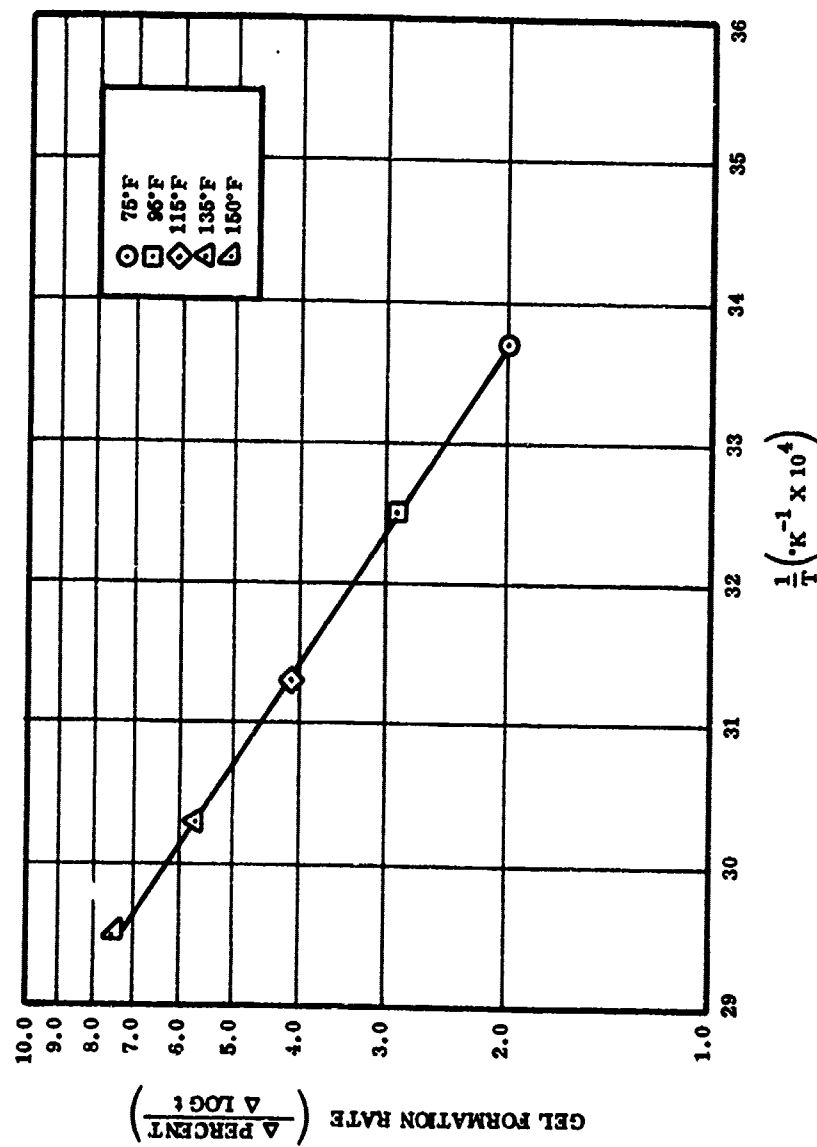
Figure 2. Temperature Dependence of the Gel Formation Rate in ANB-3066 Propellant
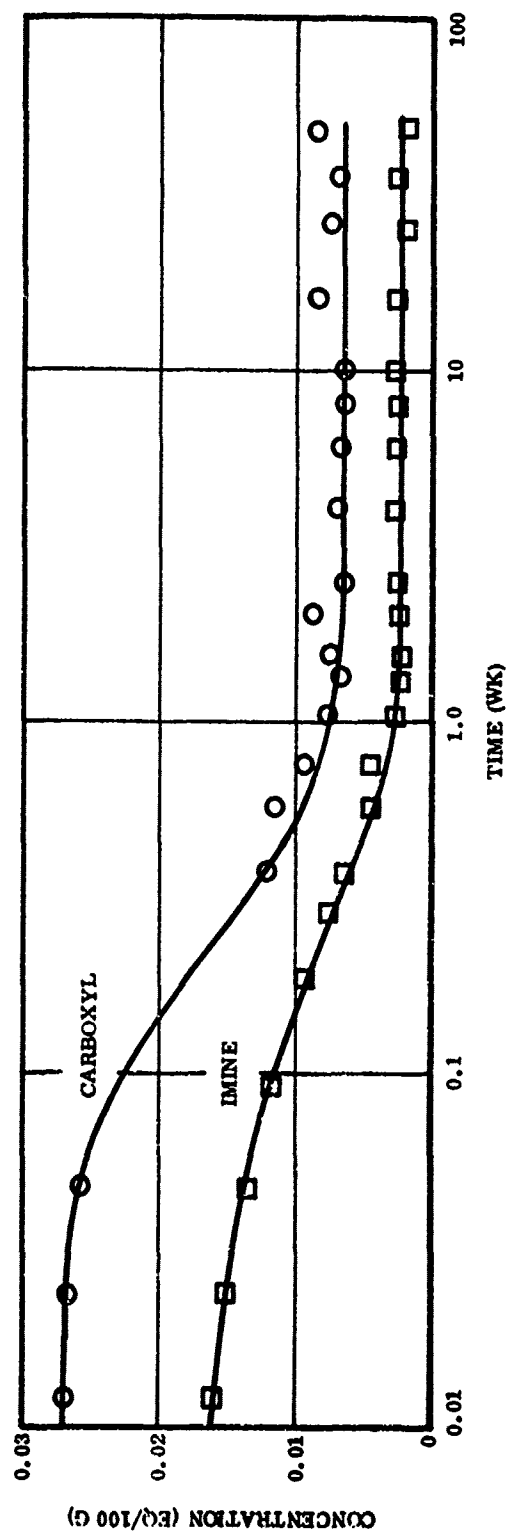
Figure 3. Concentration of Unreacted Carboxyl and Imine Groups, ANB-3066 Propellant (115°F)
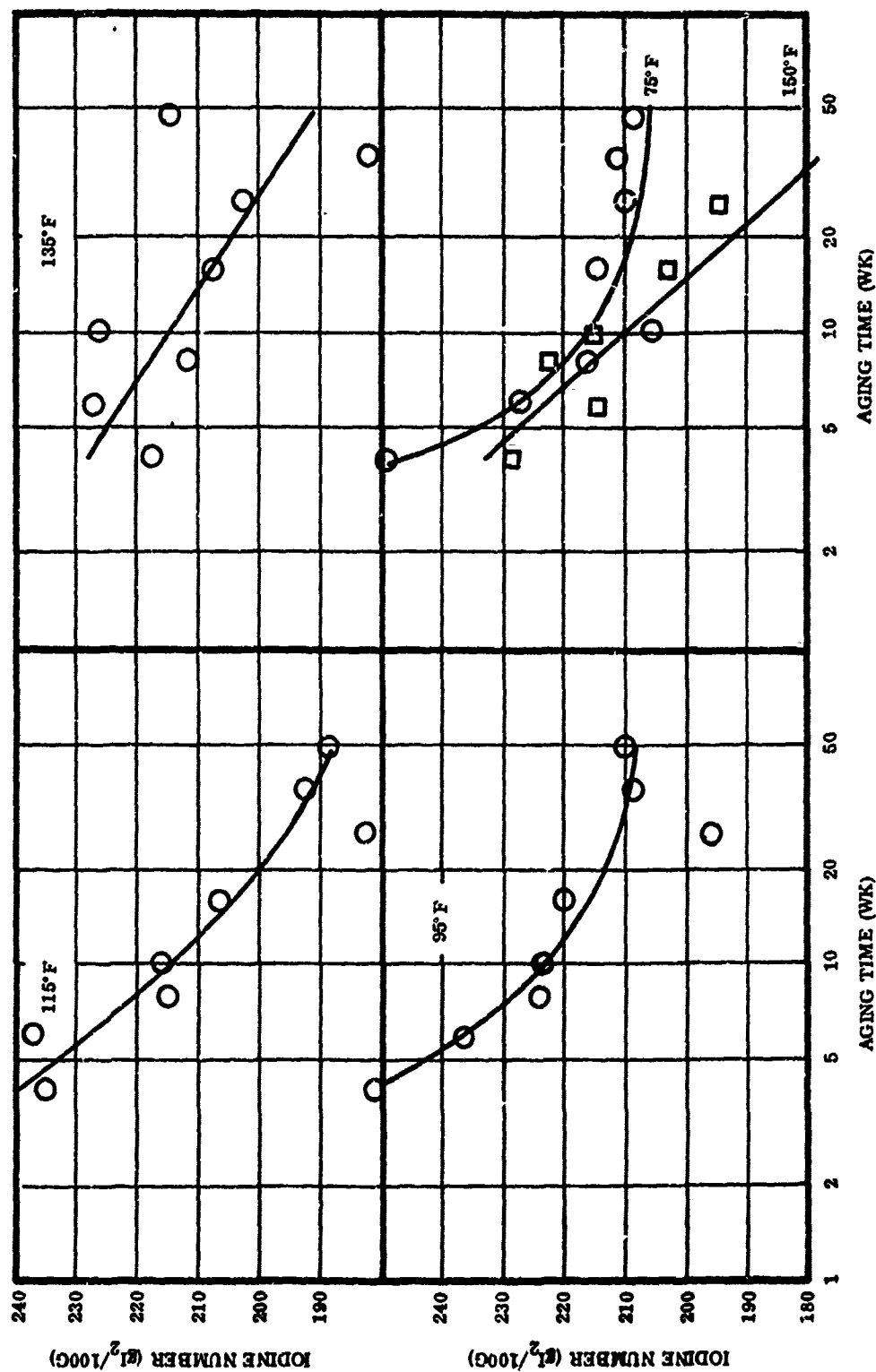
Figure 4. Change in Iodine Number With Aging Time
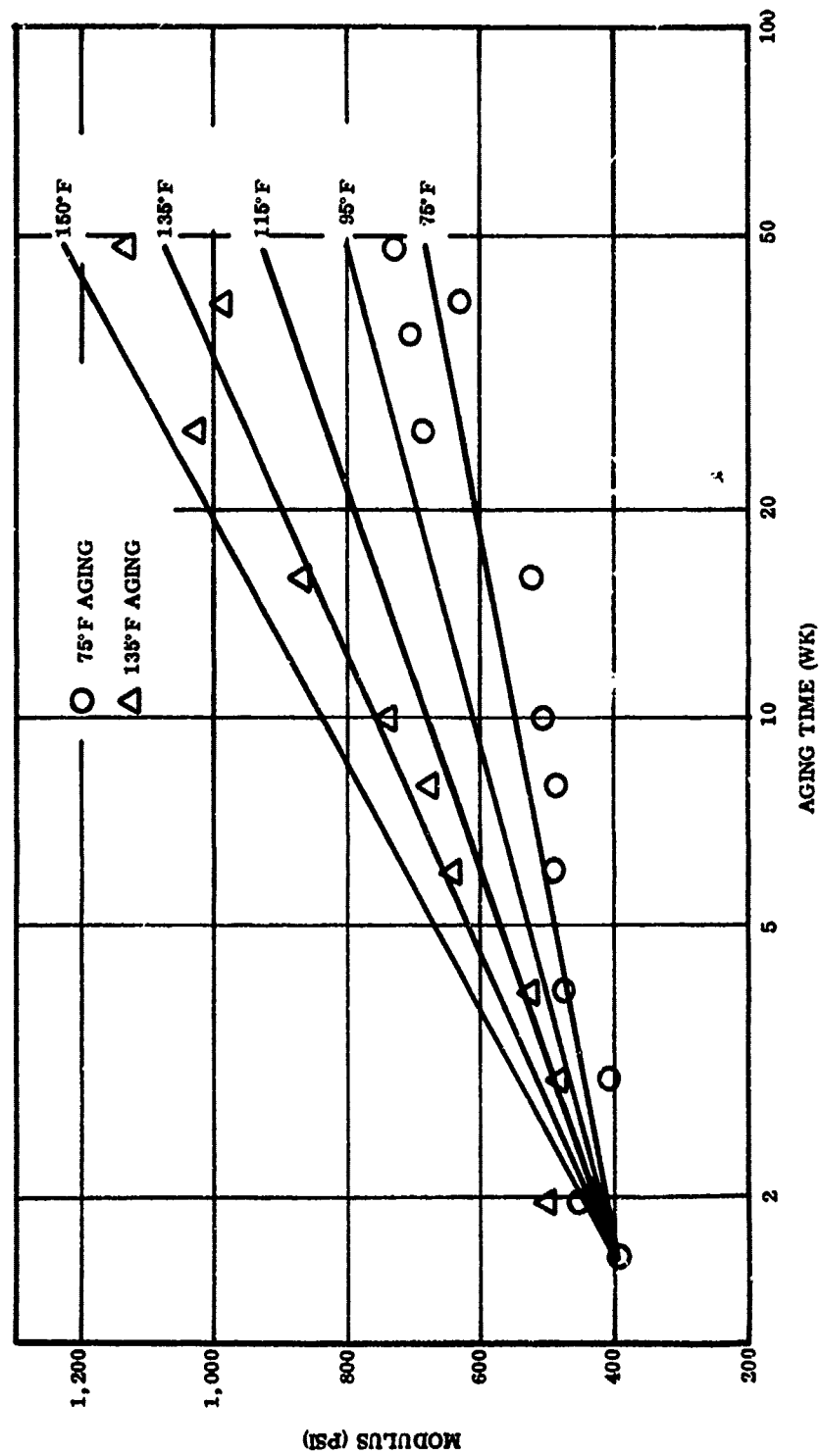
Figure 5. Effect of Aging Time and Temperature on the Modulus of ANB-3066 Propellant Tested at 2 In./Min and 75°F, Mix 7135004
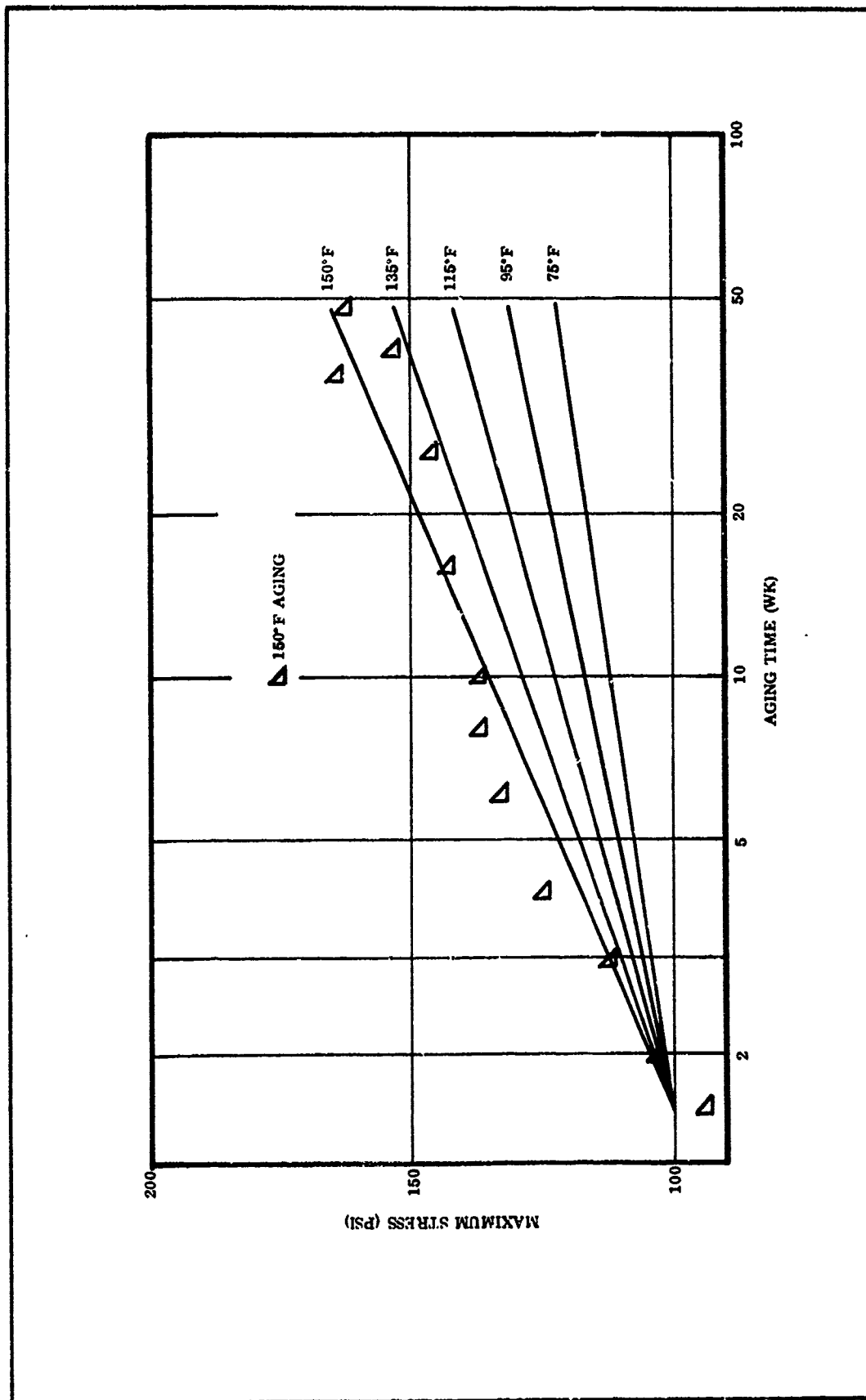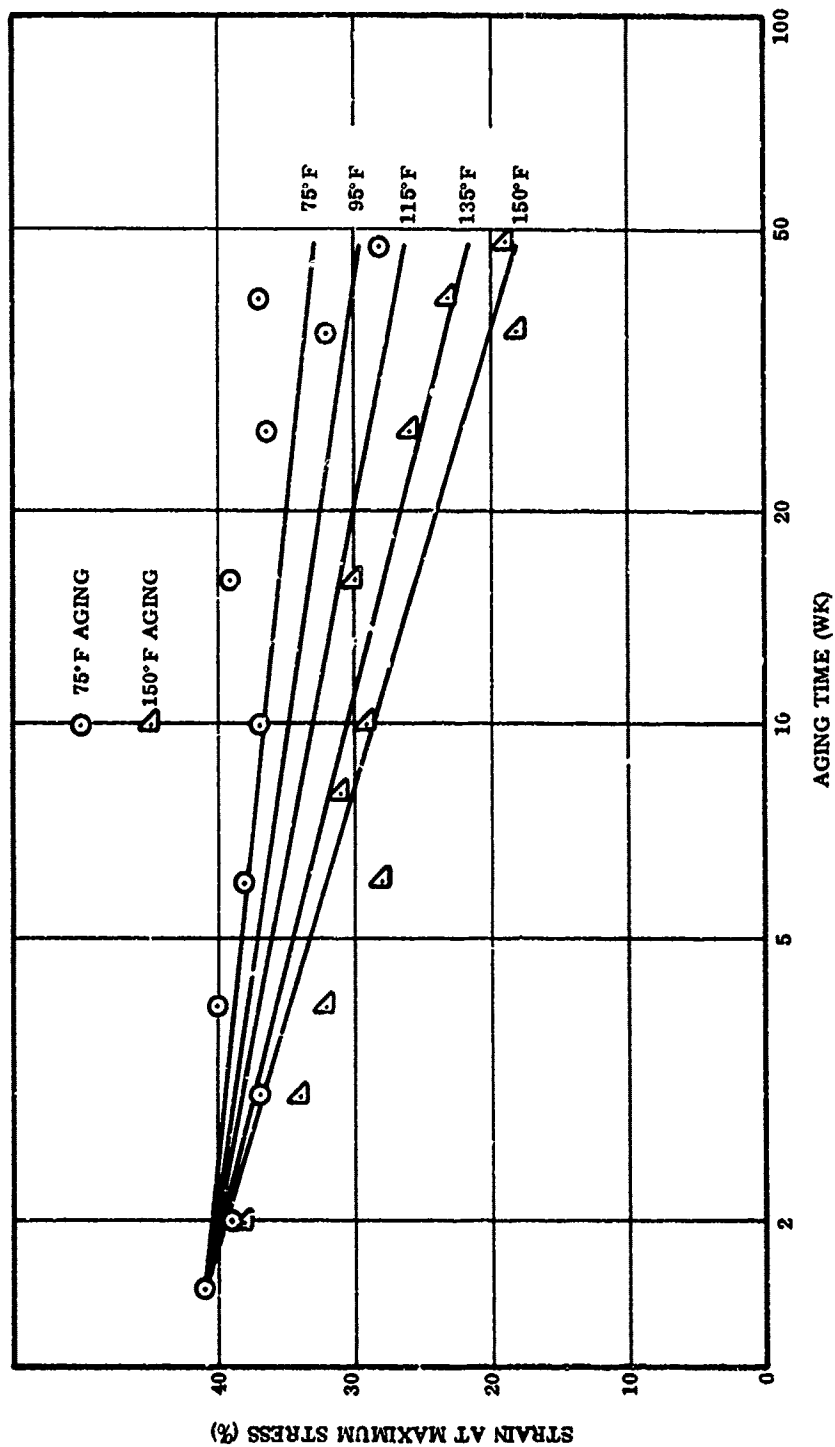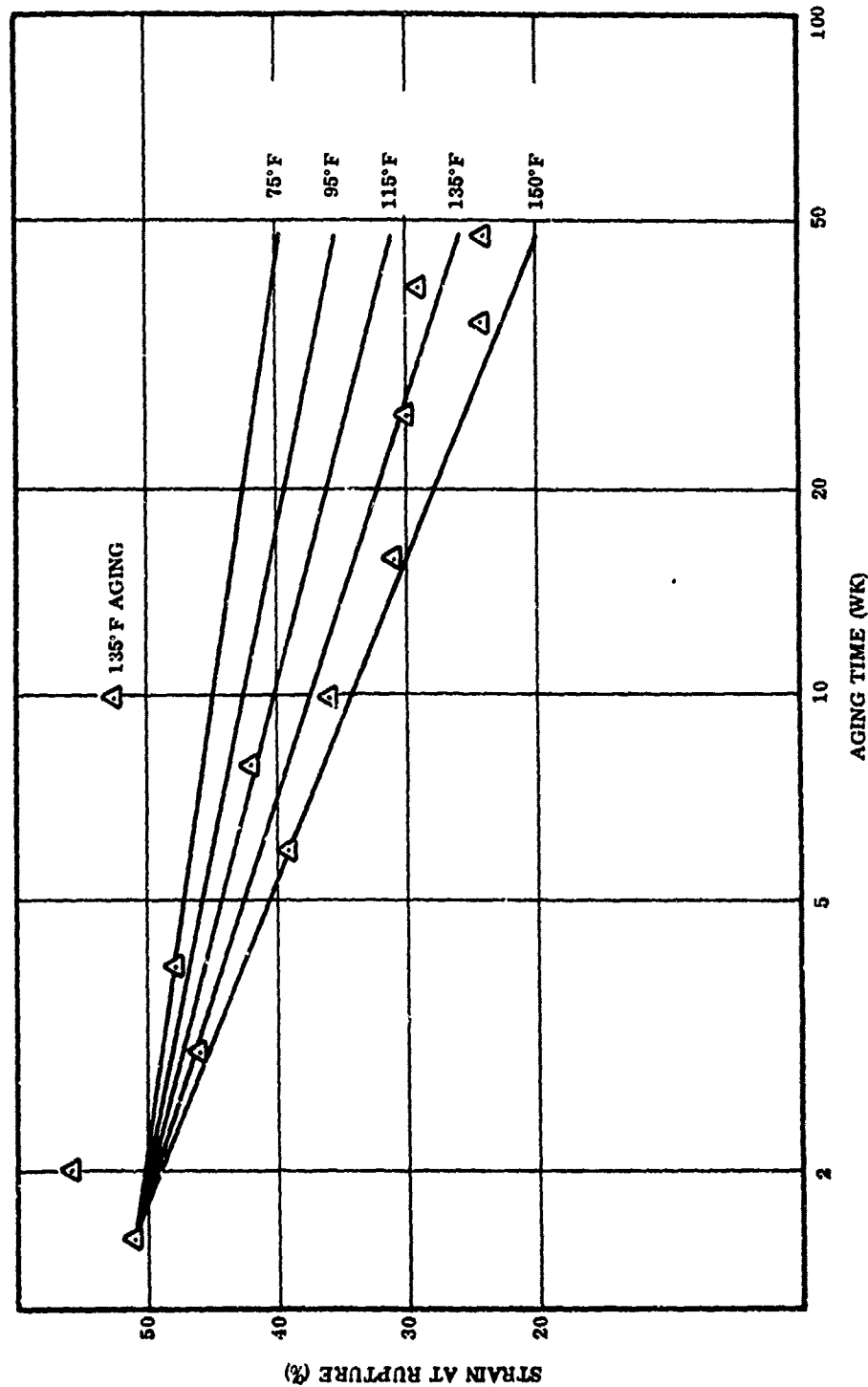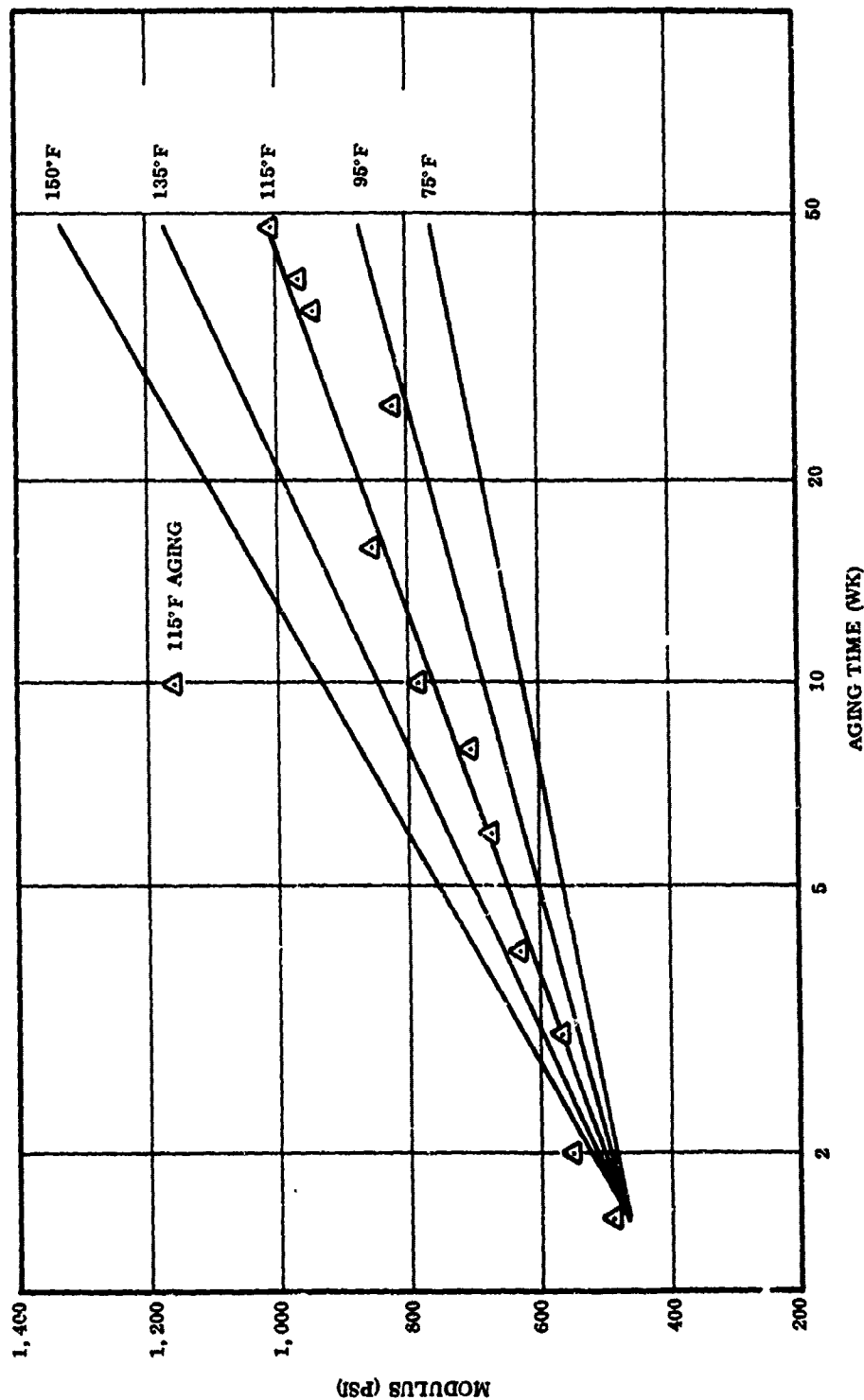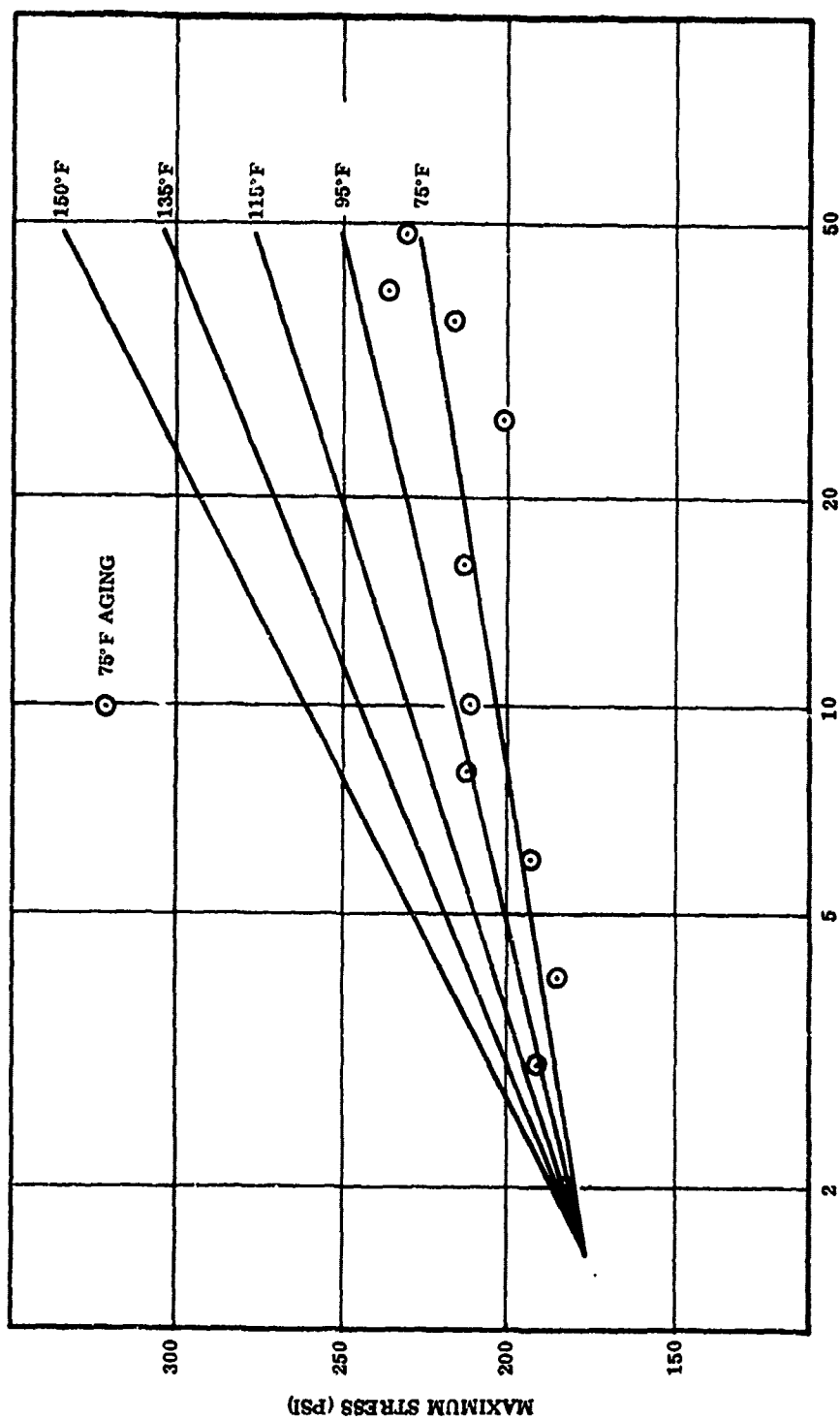
Figure 6. Effect of Aging Time and Temperature on the Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min and 75°F, Mix 7135004
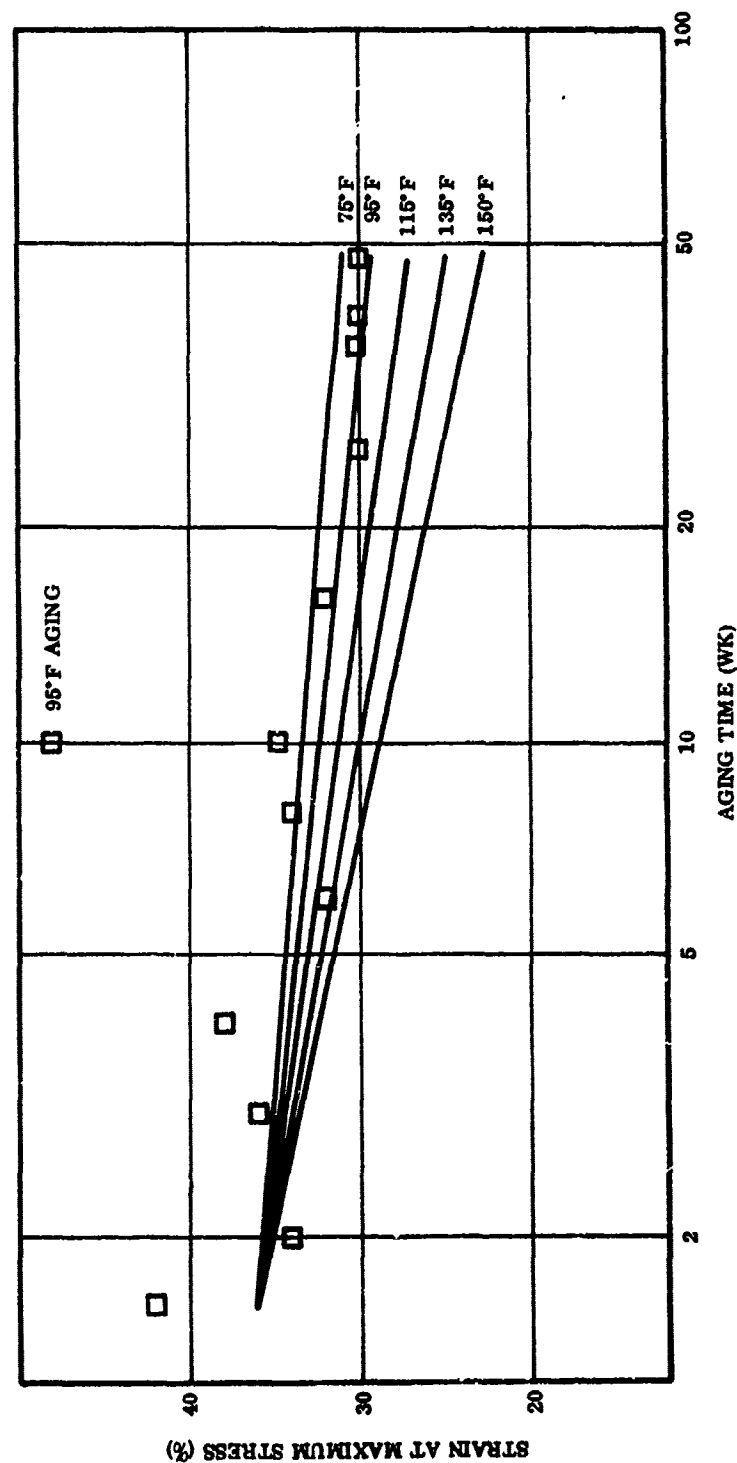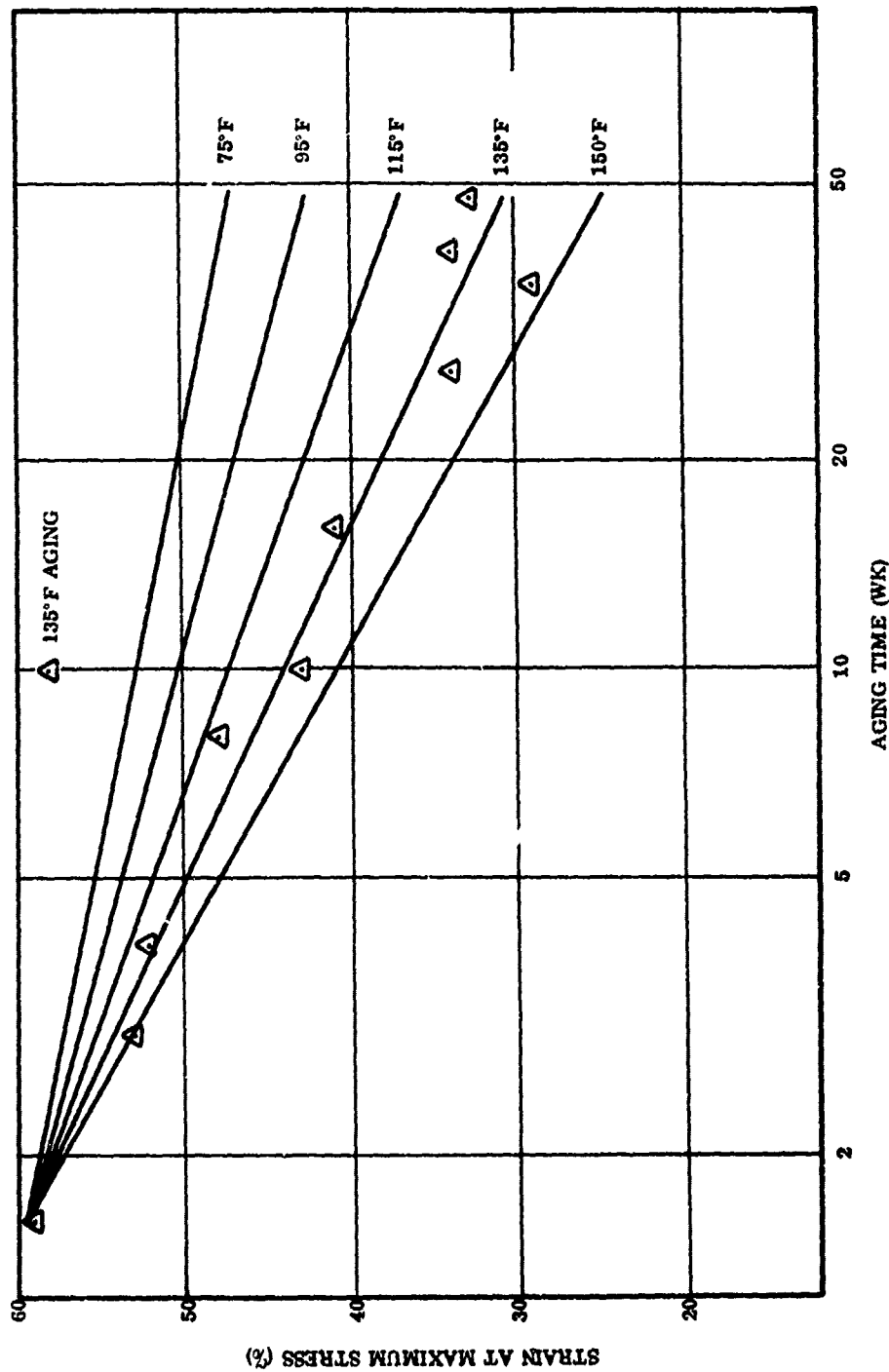
Figure 7. Effect of Aging Time and Temperature on the Strain at Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min and 75°F, Mix 715004

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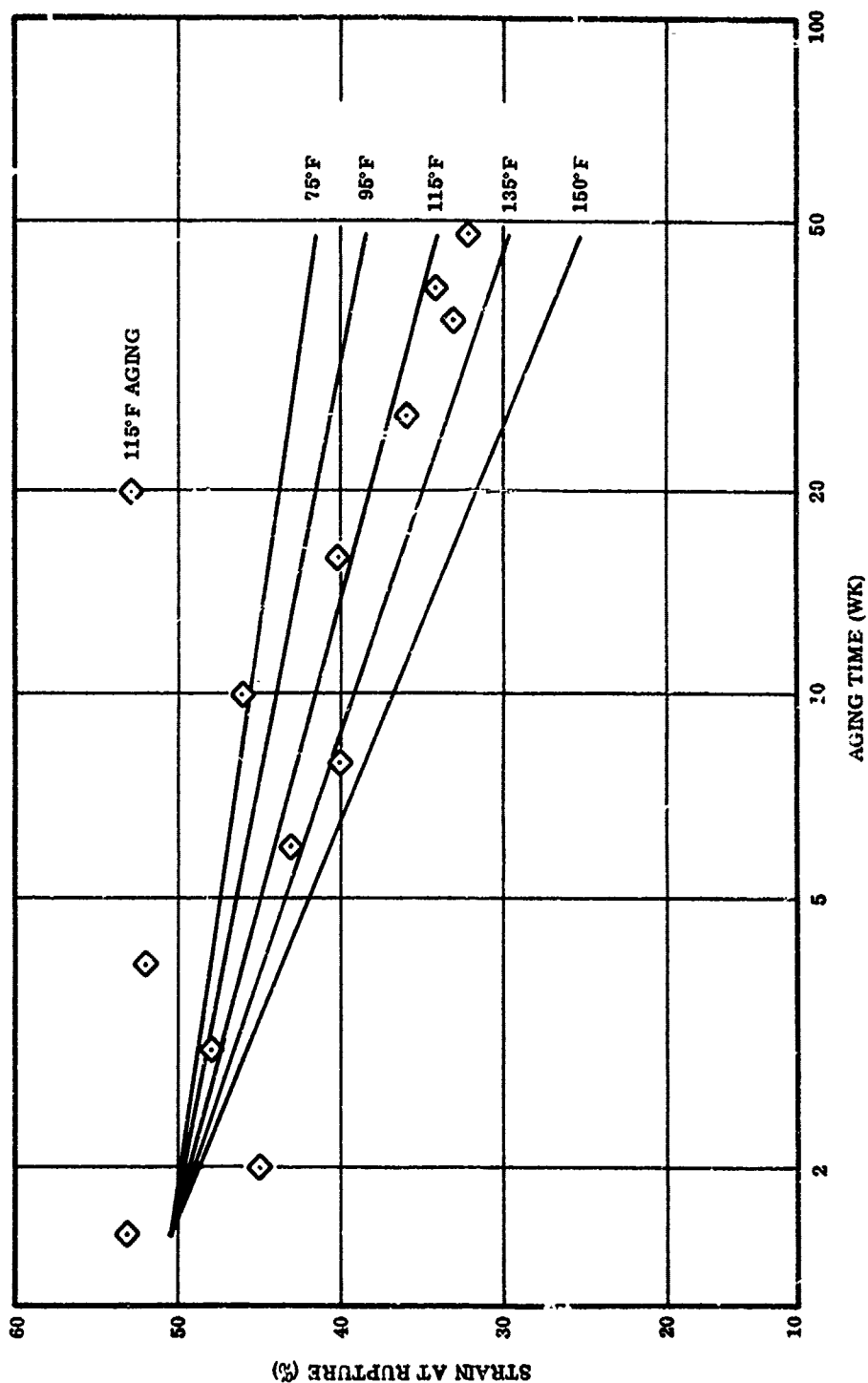
Figure 8. Effect of Aging Time and Temperature on the Strain at Rupture of ANB-3066 Propellant Tested at 2 In./Min and 75°F, Mix 7135004
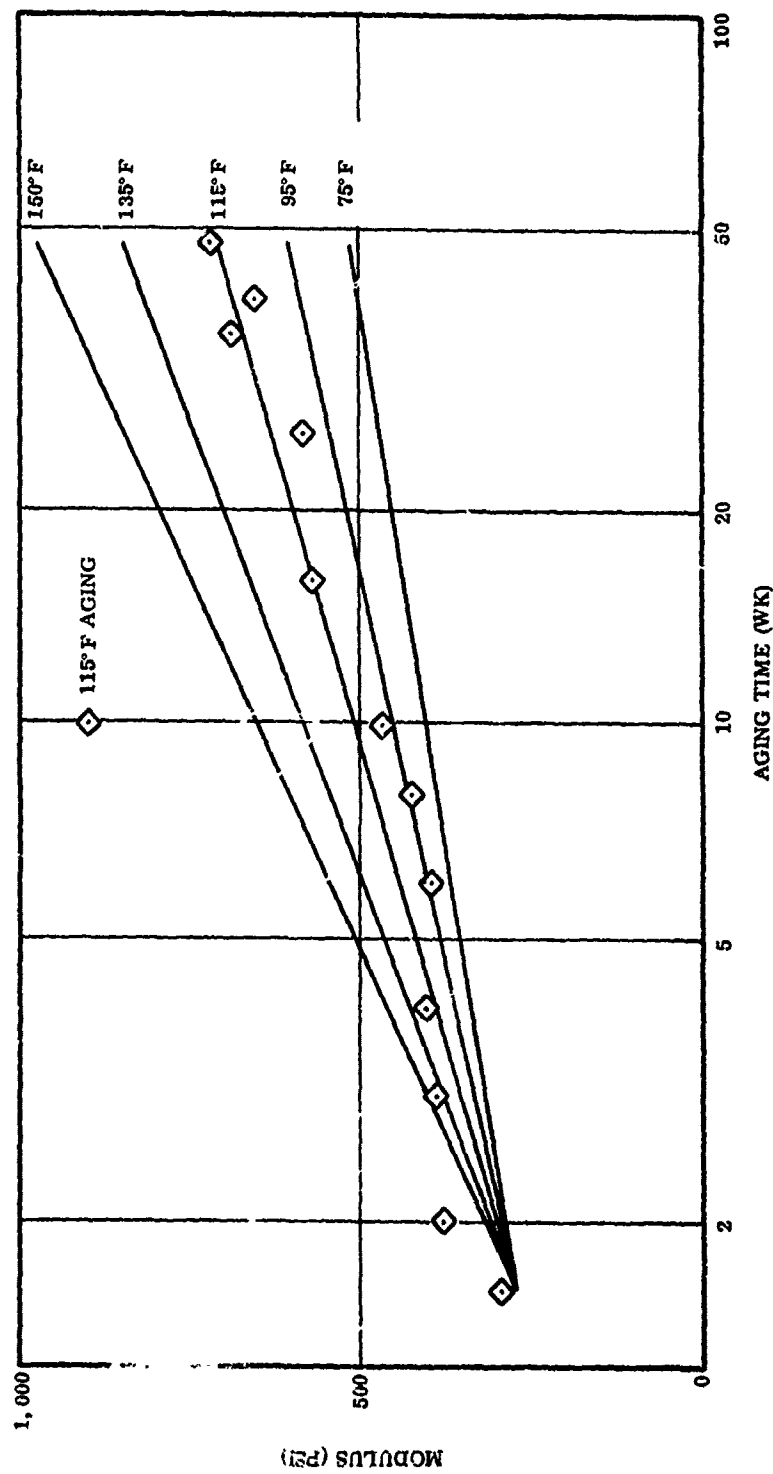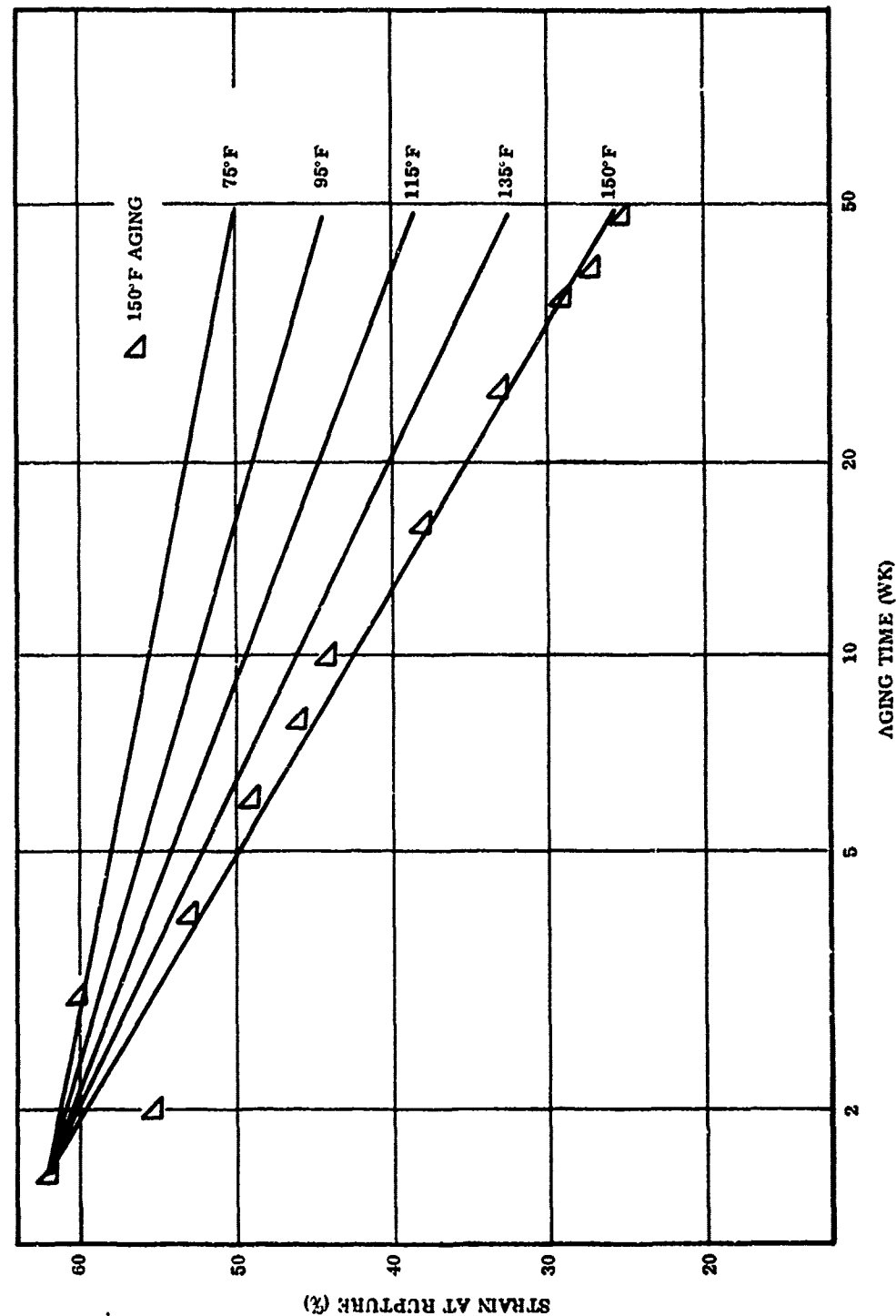
Figure 9. Effect of Aging Time and Temperature on the Modulus of ANB-3066 Propellant Tested at 2 In./Min and 125°F, Mix 7135004
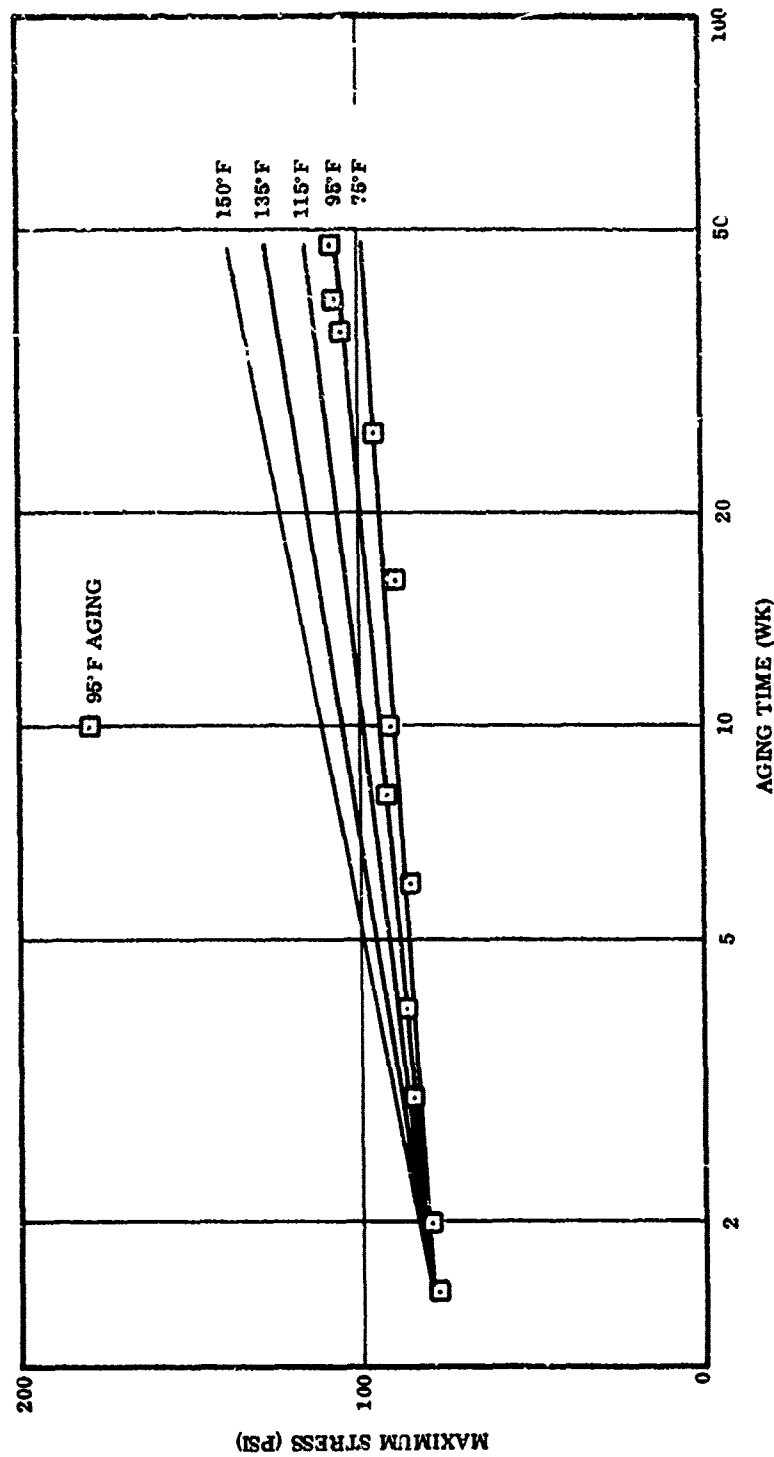
Figure 10. Effect of Aging Time and Temperature on the Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min and 25°F, Mix 7135004

Figure 11. Effect of Aging Time and Temperature on the Strain at Maximum Stress for ANB-3066 Propellant Tested at 2 In./Min and 125°F, Mix 7135004

Figure 12. Effect of Aging Time and Temperature on the Strain at Rupture for ANB-3066 Propellant Tested at 2 In./Min and 125°F, Mix 7135004

Figure 13. Effect of Aging Time and Temperature on the Modulus of ANB-3066 Propellant Tested at 2 In./Min 75°F, and With 500 psi Superimposed Pressure, Mix 7135004
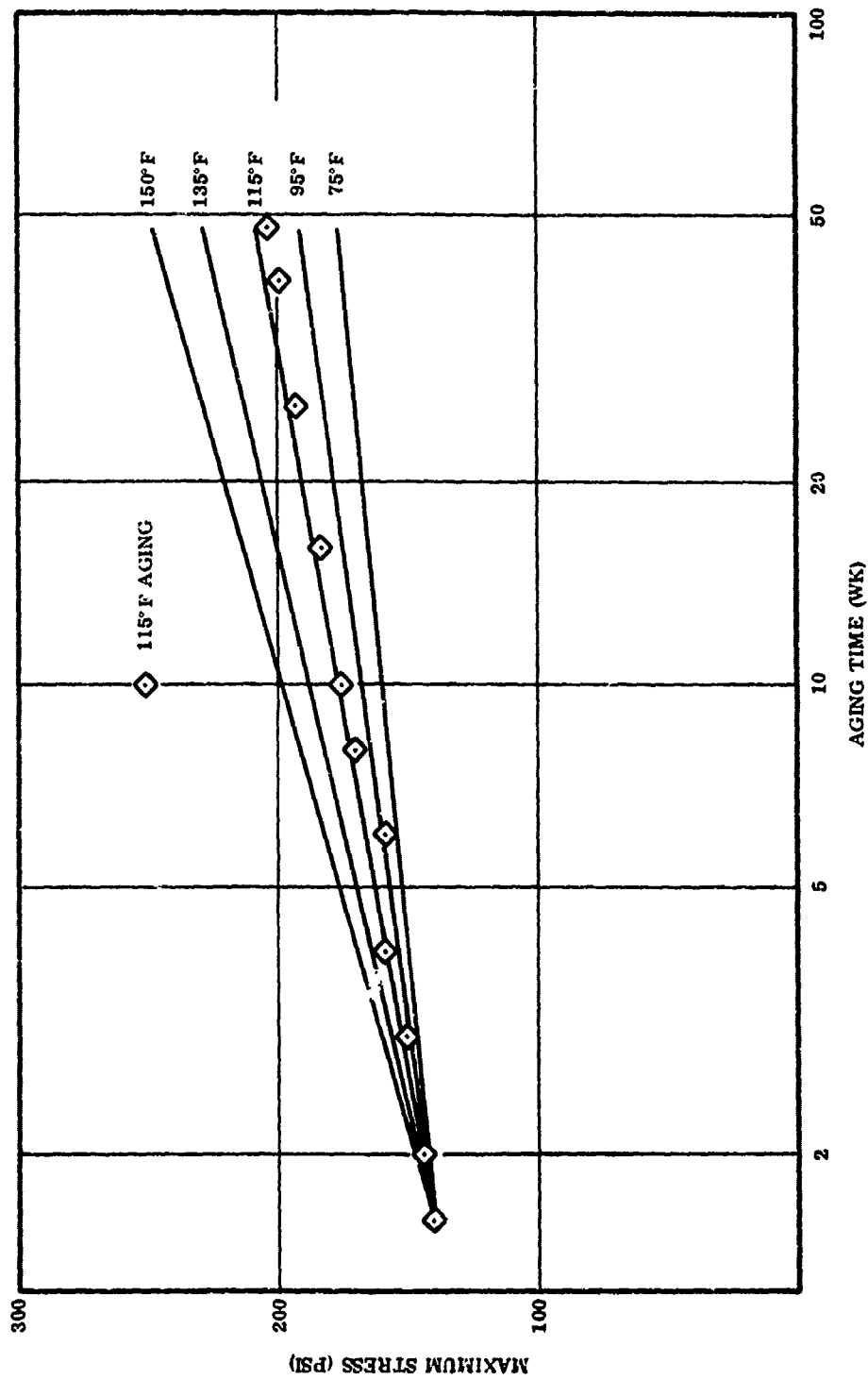
Figure 14. Effect of Aging Time and Temperature on the Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min, 75°F, and With 500 psi Superimposed Pressure, Mix 7135004
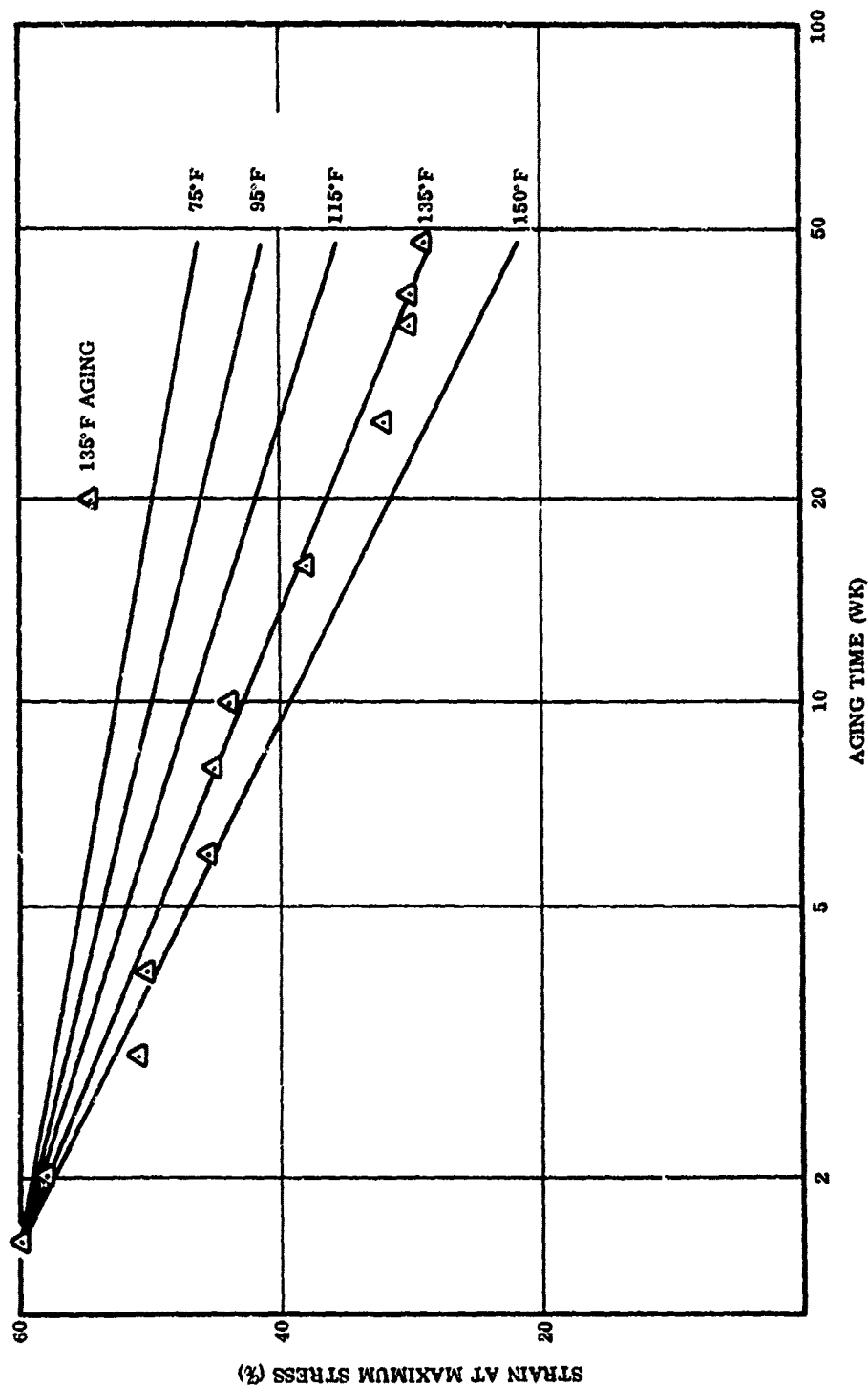
Figure 15. Effect of Aging Time and Temperature on the Strain at Maximum Stress for ANB-3066 Propellant Tested at 2 In./Min, 75°F, and With 500 psi Superimposed Pressure, Mix 7135004

Figure 16. Effect of Aging Time and Temperature on the Strain at Rupture for ANB-3066 Propellant Tested at 2 In./Min, 75°F, and With 500 psi Superimposed Pressure, Mix 7135004
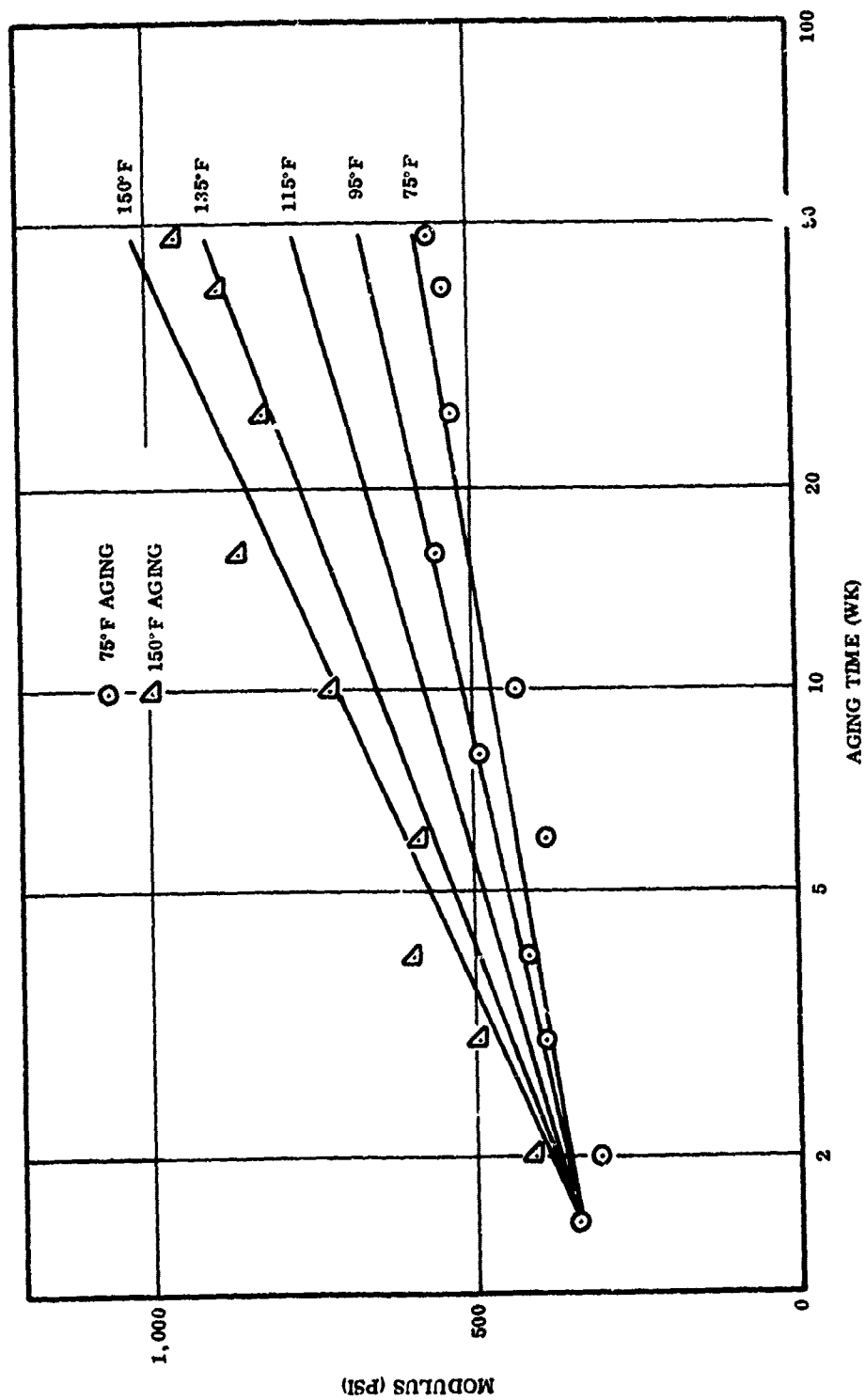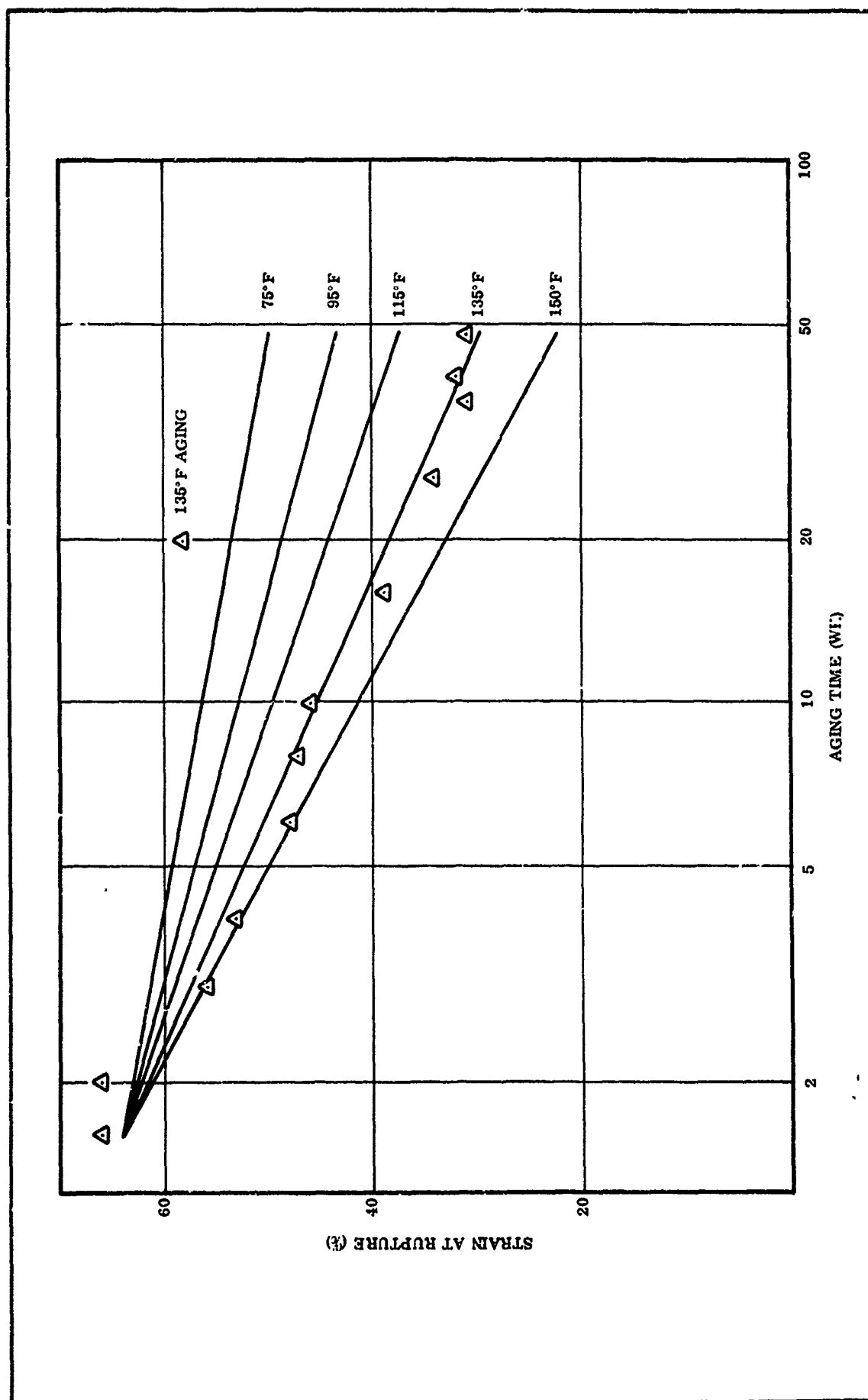
Figure 17. Effect of Aging Time and Temperature on the Modulus of ANB-3066
Propellant Tested at 2 In./Min, 125°F, and With 500 psi
Superimposed Pressure, Mix 7135004

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Figure 18. Effect of Aging Time and Temperature on the Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min, 125°F, and With 500 psi Superimposed Pressure, Mix 7135004
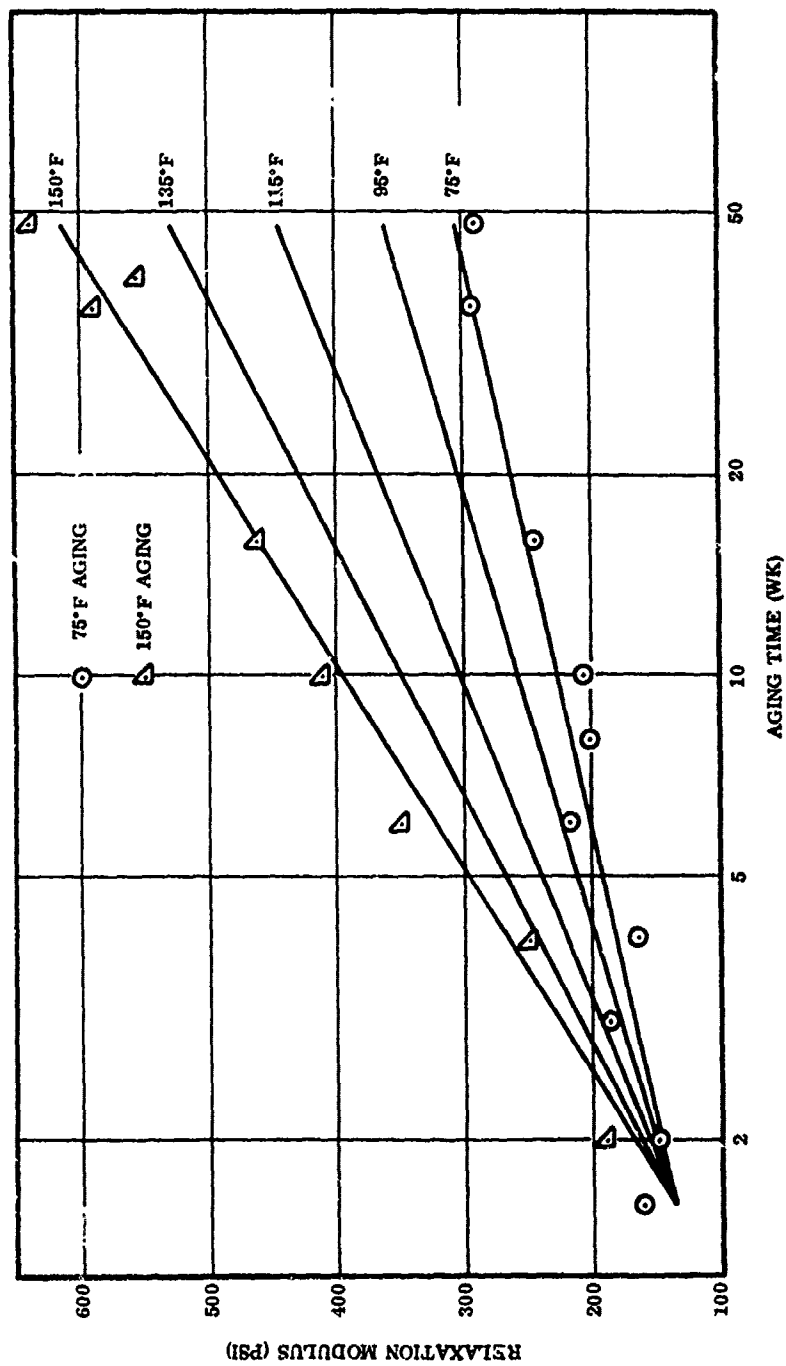
-70-

Figure 19. Effect of Aging Time and Temperature on the Strain at Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min, 125°F, and With 500 psi Superimposed Pressure, Mix 715004

Figure 20. Effect of Aging Time and Temperature on the Strain at Rupture of ANB-3066 Propellant Tested at 2 In./Min. 125°F, and With 500 psi Superimposed Pressure, Mix 7135004

Figure 21. Effect of Aging Time and Temperature on the Relaxation Modulus for ANB-3066 Propellant Tested at 2 Percent Strain and 10,000 Seconds at 75°F, Mix 7135004
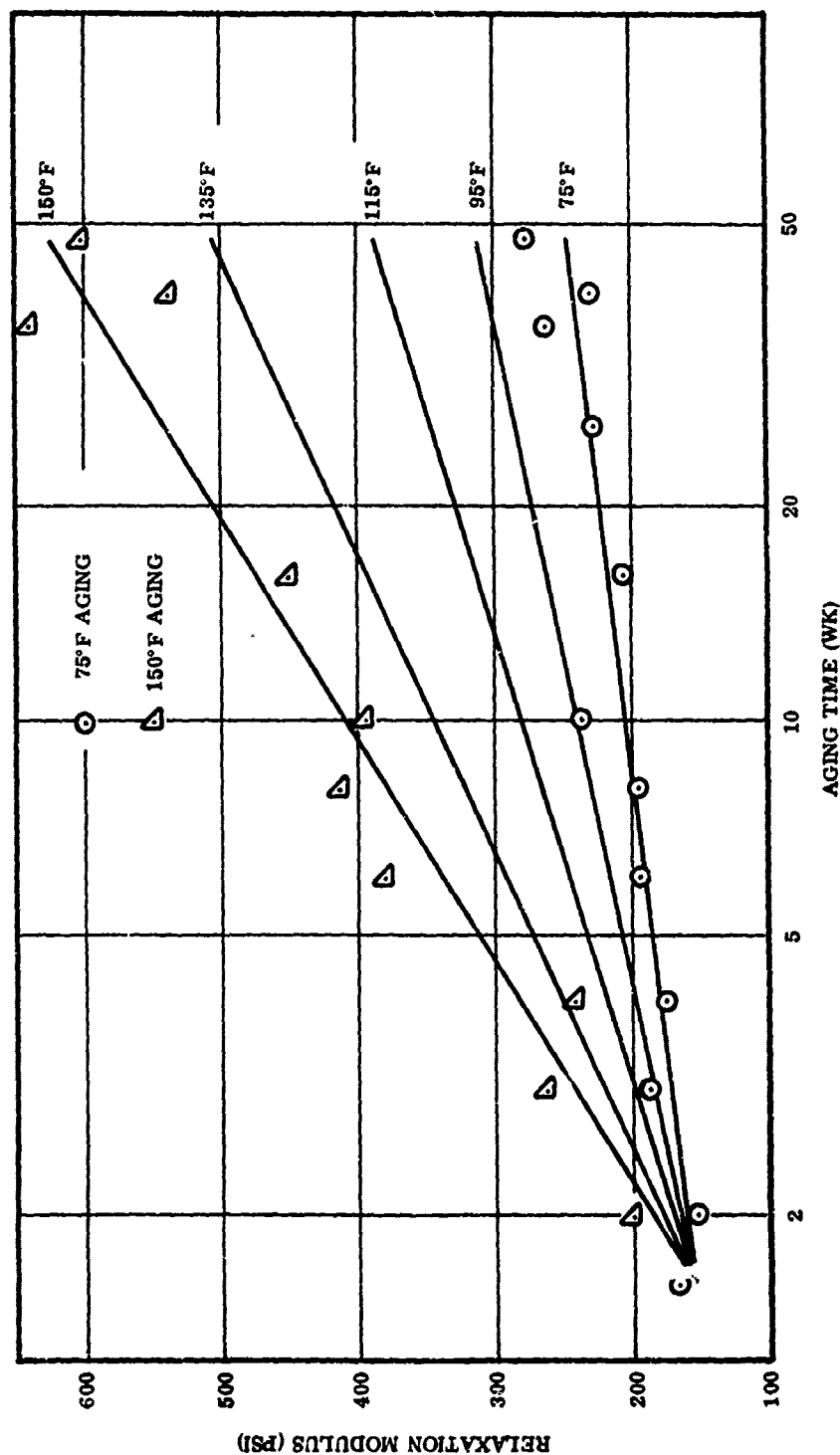
-73-

Figure 22. Effect of Aging Time and Temperature on the Relaxation Modulus for ANB-3056 Propellant Tested at 2 Percent Strain and 10,000 Seconds at 125°F, Mix 715004
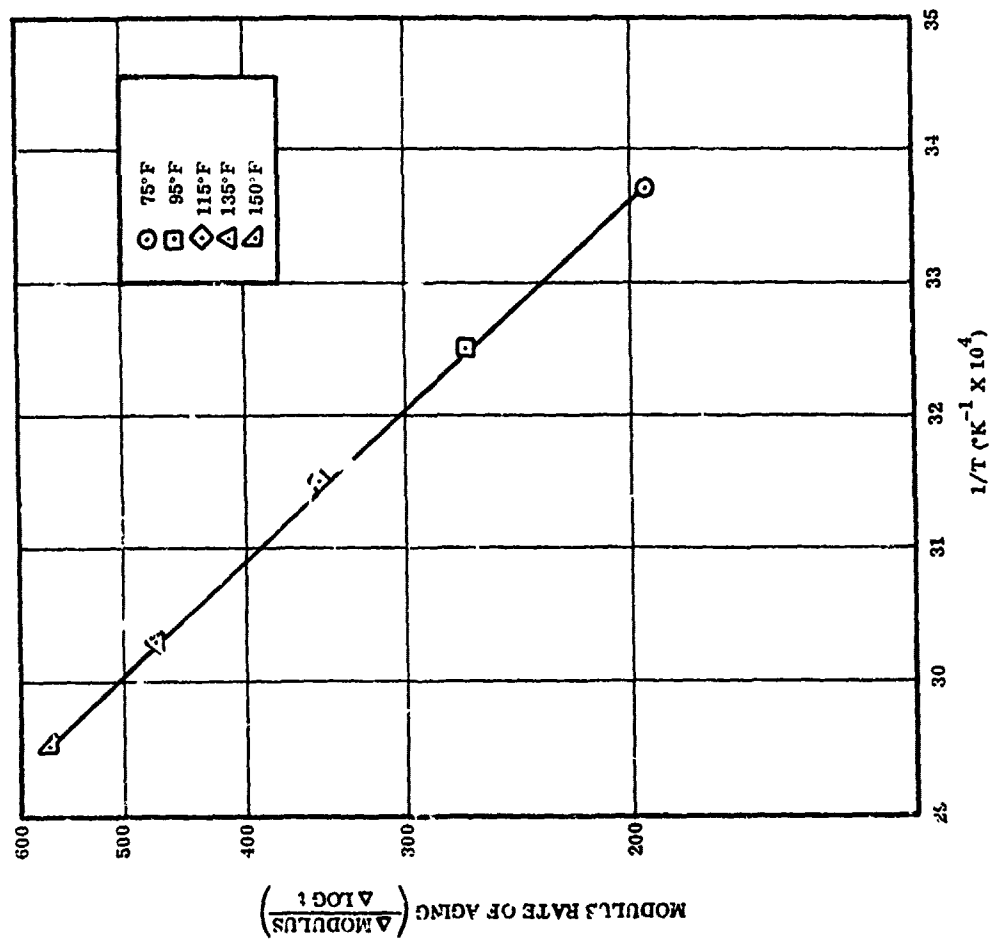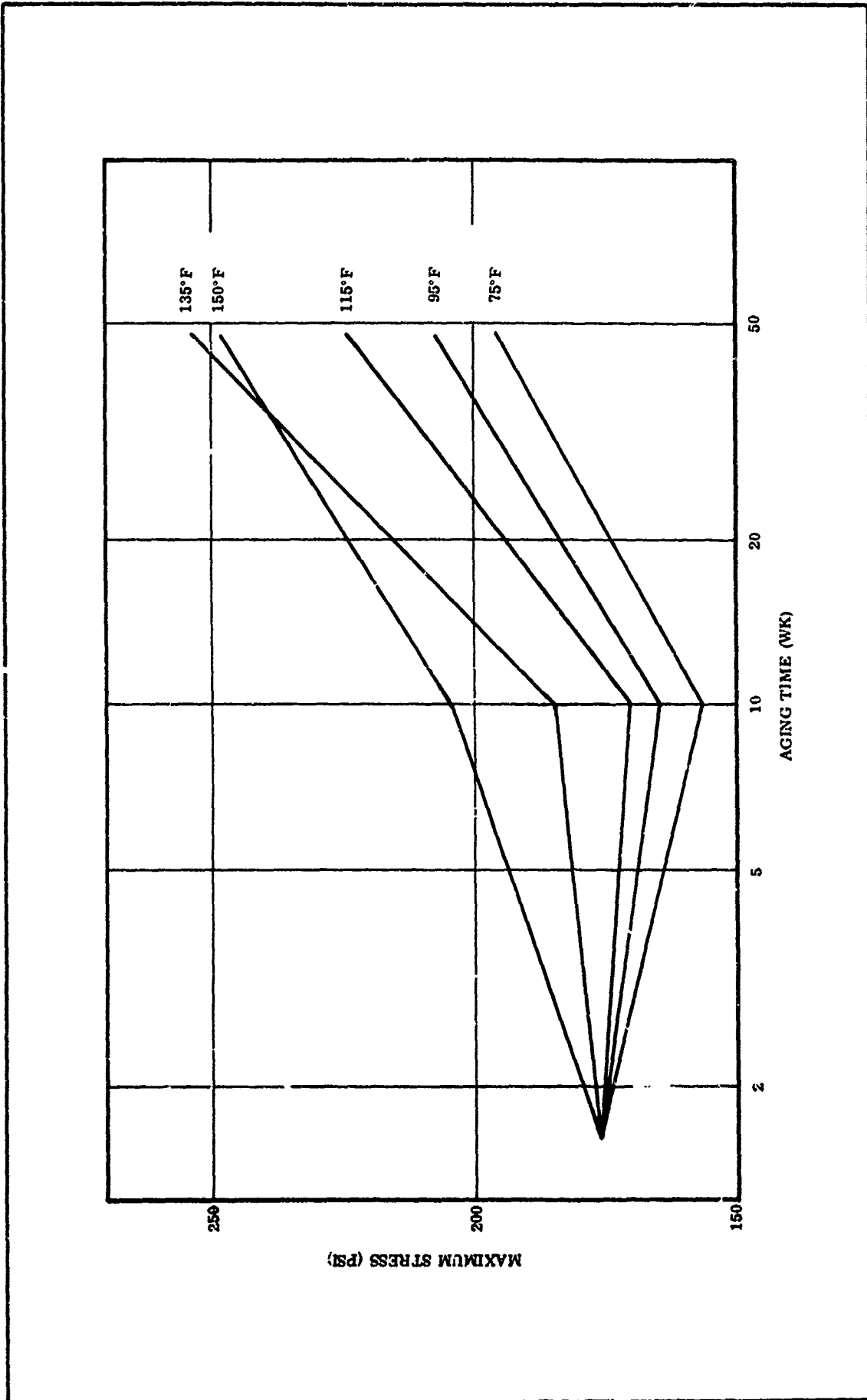
Figure 23. Temperature Dependence of Modulus Aging Rate, ANB-3066 Propellant

Figure 24. Effect of Aging Time and Temperature on the Maximum Stress of ANB-3066 Propellant Tested at 2 In./Min and 10°F, Mix 7135004
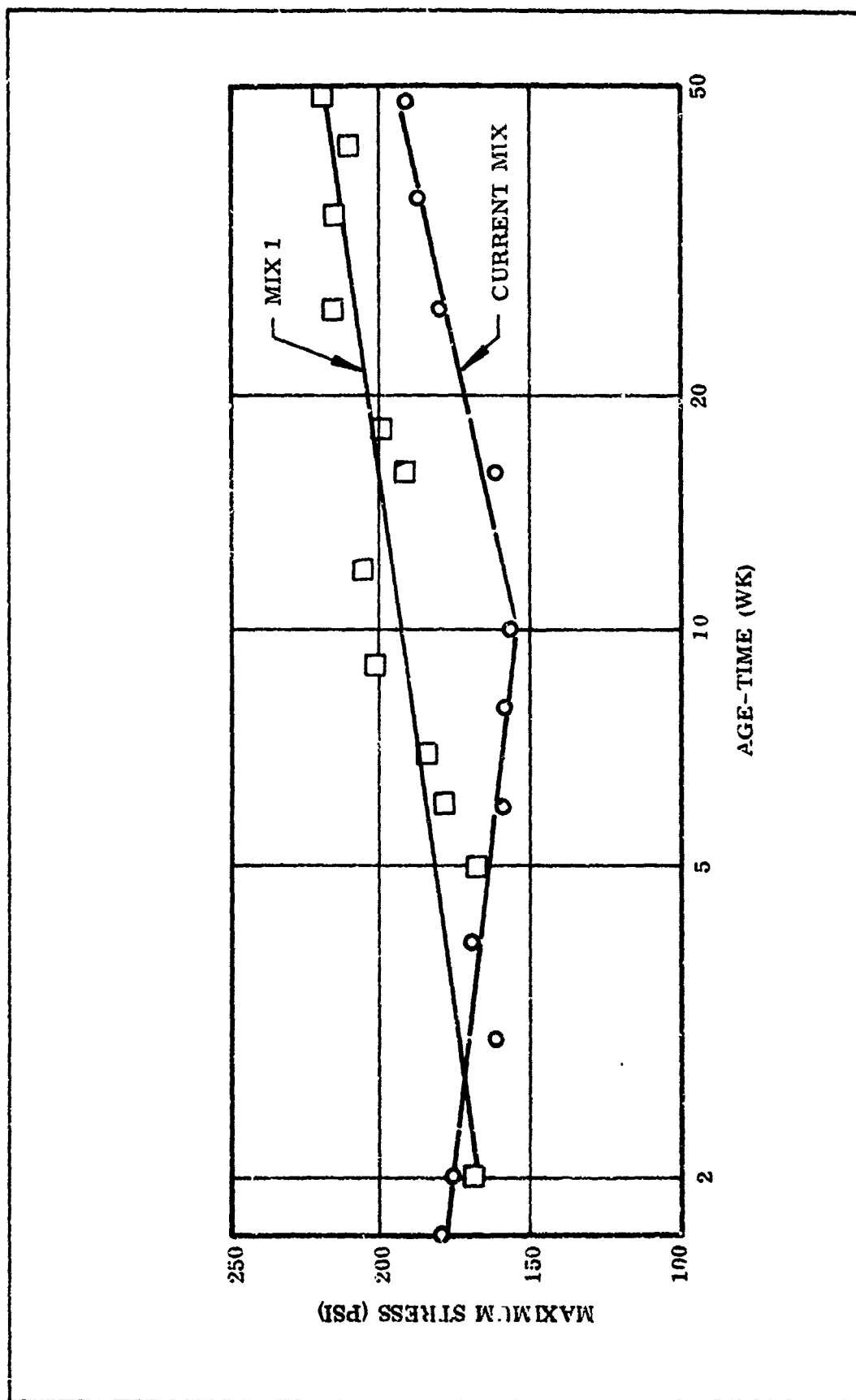
Figure 25. Comparison of the Aging Behavior of Two Different Mixes of ANB-3066 Propellant (Aged at 75° F Tested at 10° F)
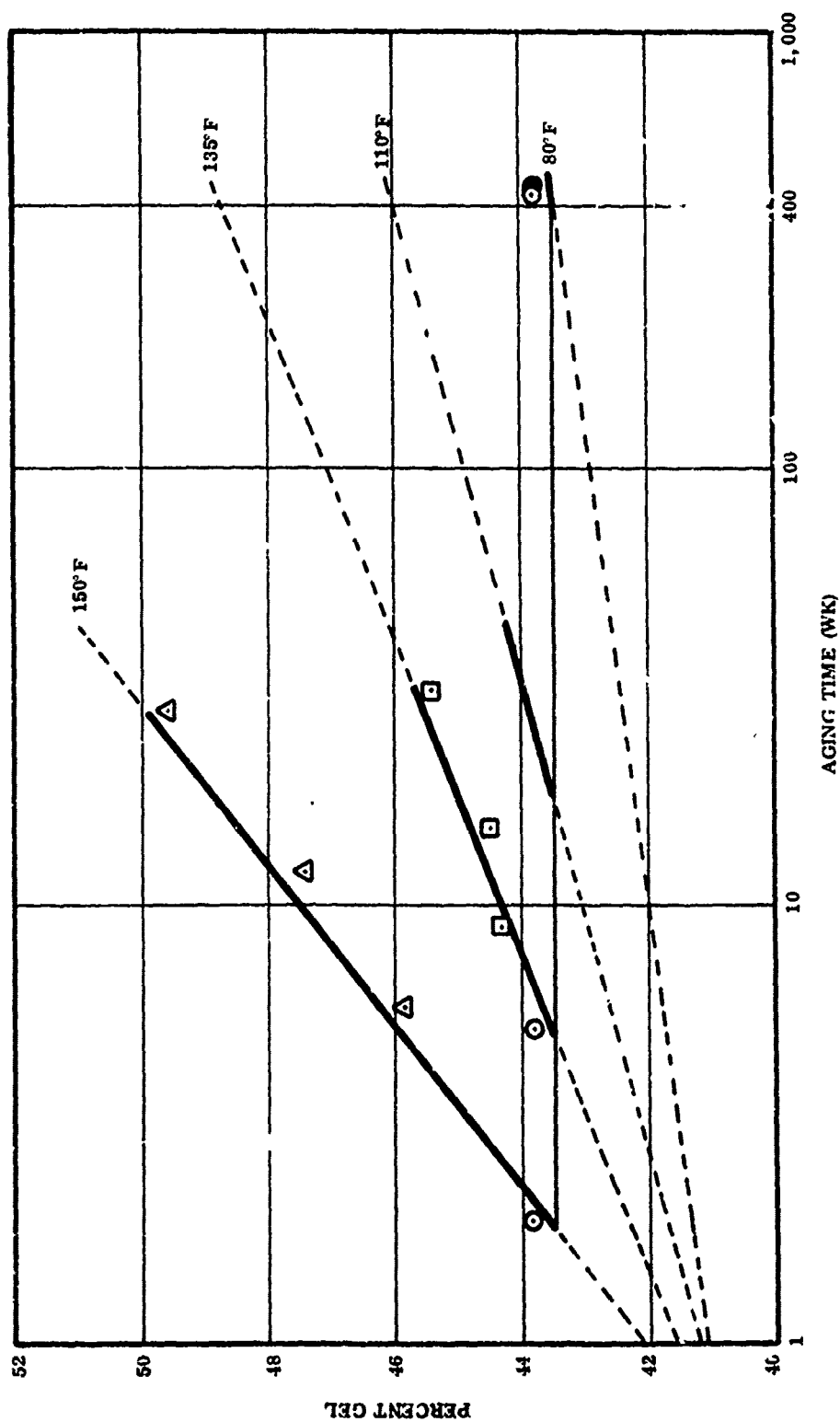
Figure 26. Percent Gel as a Function of Aging Time and Temperature, TP-H1011 Propellant
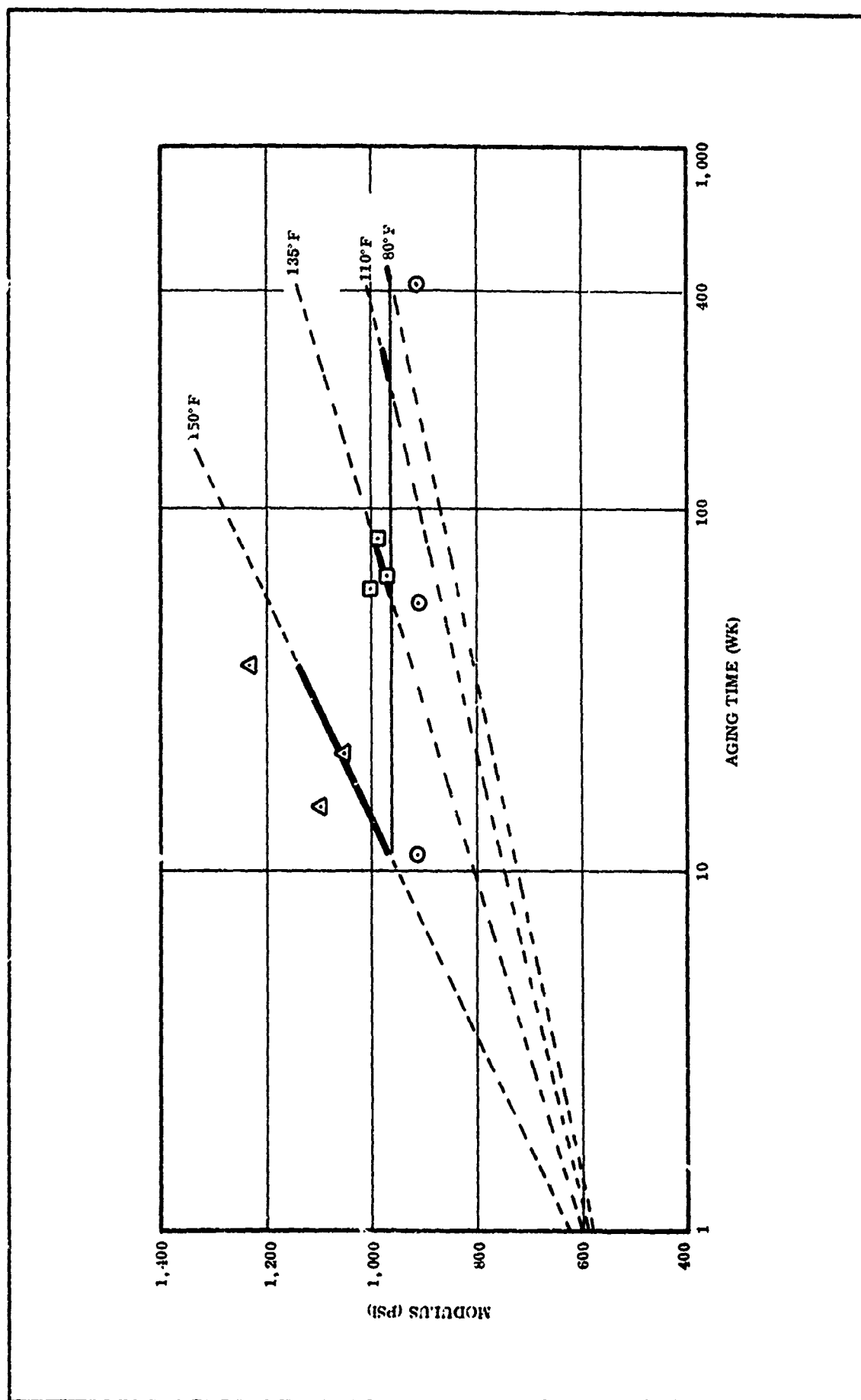
Figure 27. Modulus as a Function of Aging Time and Temperature, TP-H1011 Propellant
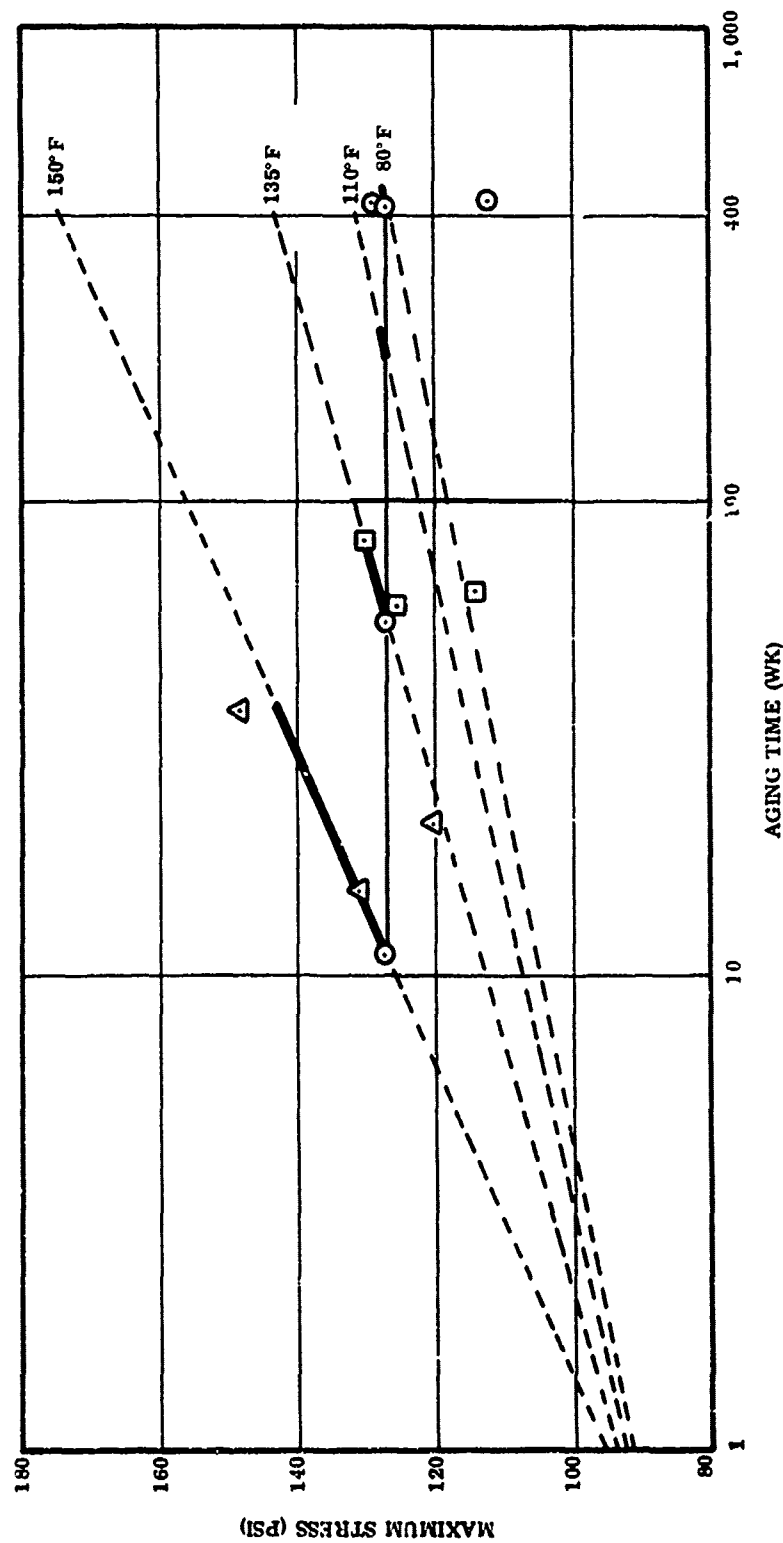
Figure 28. Maximum Stress as a Function of Aging Time and Temperature, TP-H1011 Propellant
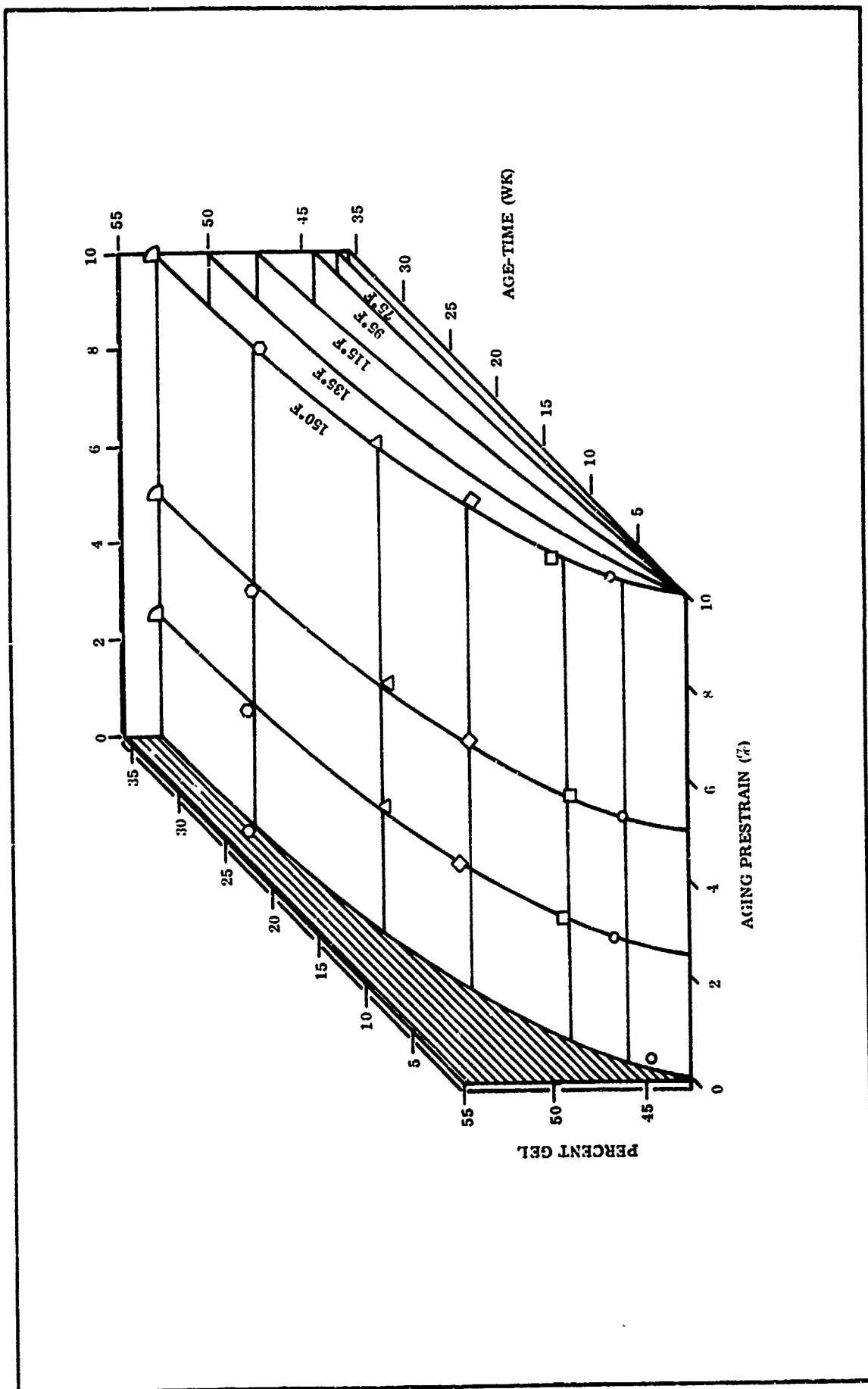
Figure 29. Effect of Aging Prestrain and Aging Time on the Percent Gel Formed in TP-H1011 Propellant Binder
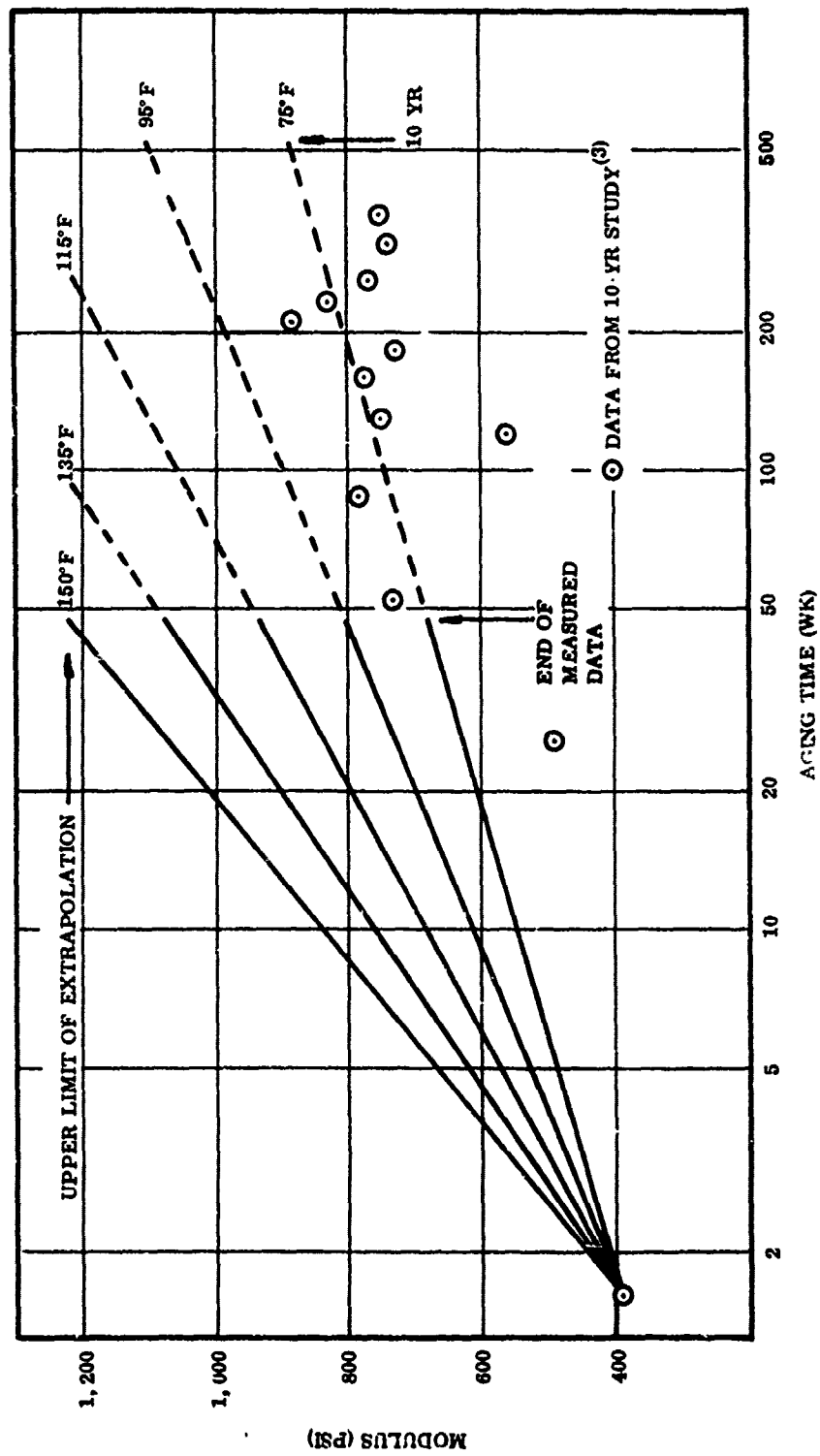
Figure 19. Comparison of the Modulus Value for ANB-3066 Propellant Predicted From 1 Yr Measured Data With Results From the 10-Yr Aging and Storage Program
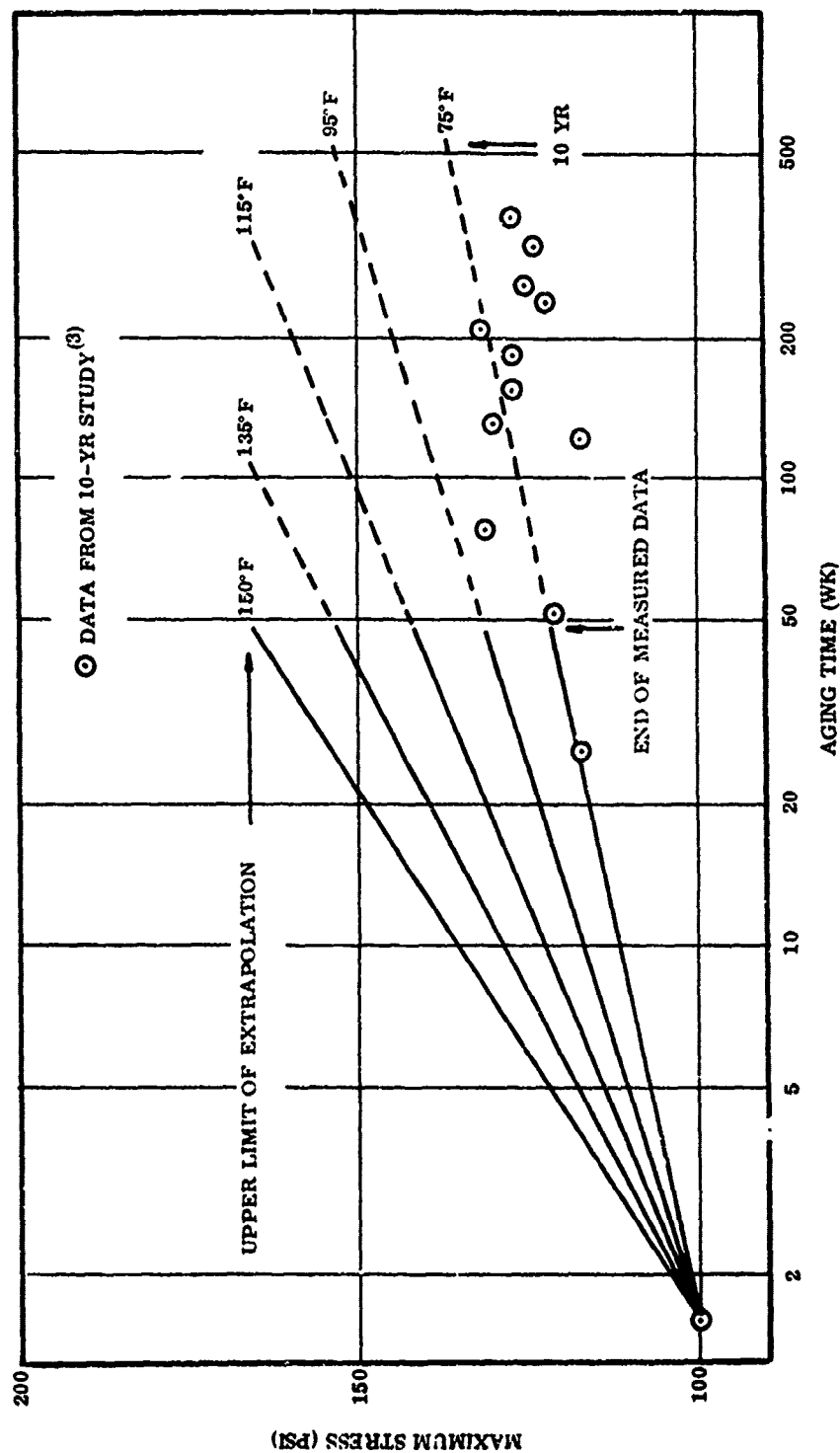
Figure 31. Comparison of the Maximum Stress Value for ANB-3066 Propellant
Predicted From 1 r Measured Data With Results From
the 10–Yr Aging and Storage Program
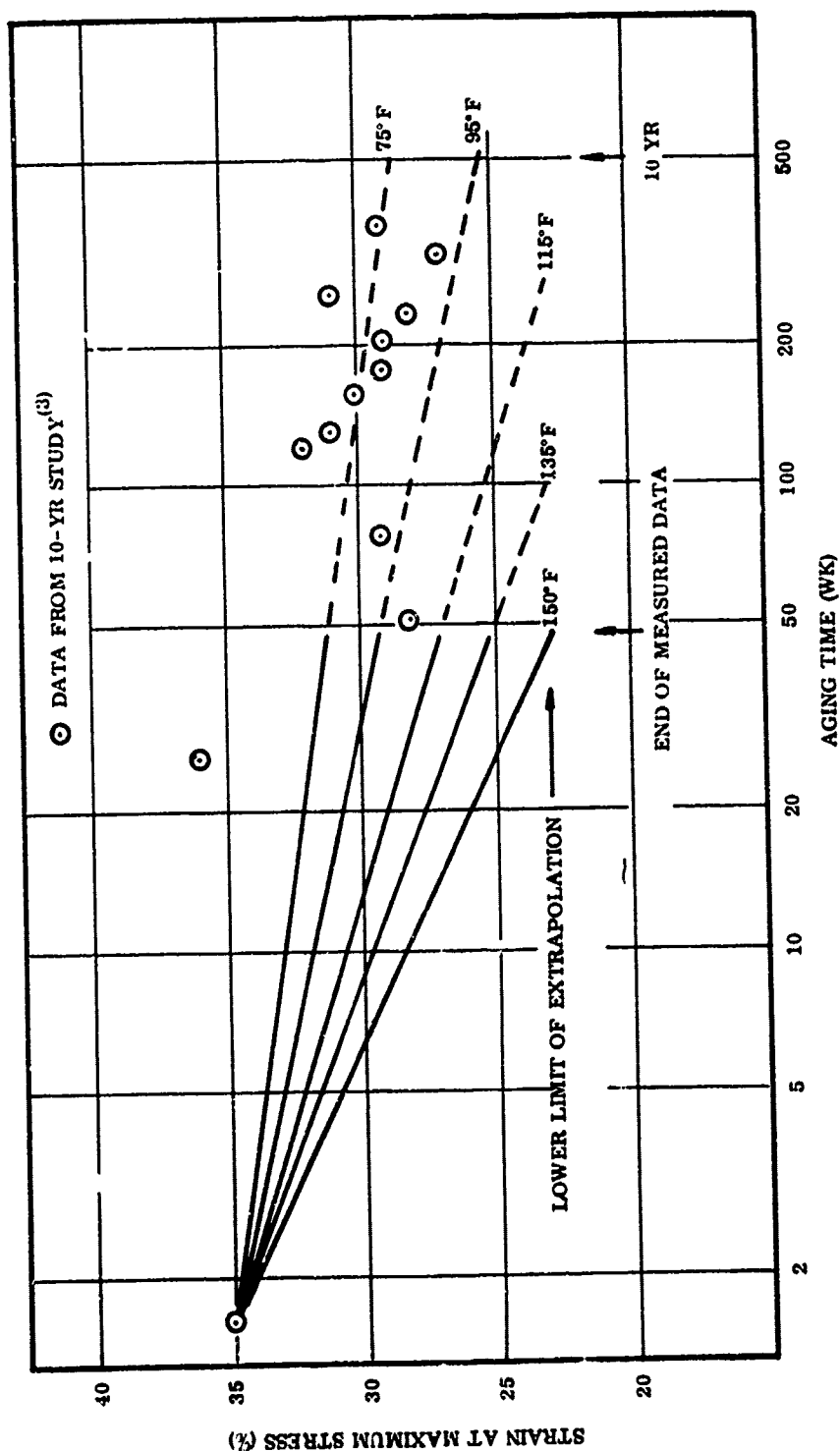
Figure 32. Comparison of the Strain at Maximum Stress Value for ANB-3066 Propellant Predicted From 1 Yr Measured Data With Results From the 10-Yr Aging and Storage Program

APPENDIX A

CARBON-13 MAGNETIC RESONANCE STUDY OF THE CURING AND AGING OF ROCKET PROPELLANT POLYMERS

I. Introduction

Since the chemical changes which influence the macroscopic physical properties of cured polymers must occur at the molecular level, it is logical to attempt to investigate the microscopic characteristics of such systems. Carbon-13 magnetic resonance (cmr) is an obvious tool to utilize since the fundamental, back-bone structure of the polymers of interest is composed almost solely of carbon. Although carbon-13 is of low natural abundance (1.1%) and small magnetic moment, compared to hydrogen which is more widely known for its use in magnetic resonance studies, difficulties in observing carbon-13 resonance spectra have been greatly reduced in recent years by instrumental advances which allow signal averaging of free induction decays followed by Fourier transform, a mathematical operation which converts the accumulated data from the time domain to the more traditional and more easily interpretable frequency domain. The nmr research group in the Chemistry Department at the University of Utah utilizes a Varian XL-100-15 spectrometer, which is a state-of-the-art instrument. The dedicated Varian 620-f minicomputer, associated with the XL-100 will perform an eight kiloword Fourier transform in about nine seconds. The computer has mass storage capabilities through its interface to a 2.2 megaword magnetic disk, having one fixed and one removable platter. A high power probe and pulse amplifier produce a $\pi/2$ pulse of 17 μsec for carbon-13, which adequately covers the 250 part per million (ppm) range of chemical shifts which is typically encountered for carbon-13 resonances.

II. Chemical Shifts

Carbon-13 spectra were acquired on the carbon containing compounds involved in this study in order to obtain the chemical shifts and for purposes of assigning resonance lines in mixtures of the compounds. The compounds studied were carboxyl terminated polybutadiene (CTPB), polybutene plasticiser, and HX-868 (BITA) curing agent.

i) Polybutene plasticiser. The C-13 spectrum of this compound is very complex, exhibiting at least 50 resonance lines, all but a few of which are concentrated in the aliphatic region. Many of the lines overlap severely, forming a broad band of resonances. Such a spectrum must result from numerous units of short and intermediate length aliphatic chains connected in many combinations. Less than 1% of the carbons present resonate in the olefinic region, probably indicating the presence of some residual, unreacted butene. A second small band of resonances (< 5%) which lies outside the aliphatic region is unassigned; it falls in that part of the spectrum commonly associated with alcohols or ethers. The chemical shifts of this substance are not reported here because they are so numerous and such a tabulation is not useful. Because of the complexity of its spectrum, it was desirable to avoid adding this material to any of the polymer samples studied.

ii) HX-868 (BITA) curing agent. The cmr lines of this compound were assigned using off resonance techniques. The chemical shifts are given in Table I. The numbering system is indicated in Fig. 1. A substantial impurity was found in this sample, having two prominent resonance lines, one of which indicated the presence of carboxyl, the other being in the aromatic or olefinic region of the spectrum. The amount of impurity is difficult to estimate because its relaxation characteristic differ greatly from those of the BITA compound; however, it may exceed 5%.

iii) CTPB. The polymer was run both as a neat liquid and as a solution. The polymer is depicted in Fig. 2 and the chemical shifts are given in Table II. Assignments given in Table II were made on the basis of off-resonance spectra, line intensities, and by use of chemical shift parameters. The assignments of smaller resonance lines in the olefinic region are somewhat tentative due to the small range which they cover.

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Long term averaging techniques were employed with the neat polymer to locate

the resonance of the carboxyl end group. This resonance is very small and has

relatively unfavorable relaxation characteristics, so it is difficult to locate.

In observing the end group resonance at least seven other lines of similar in-

tensity were observed plus a number of other, smaller lines. These signals may

result from other carbons associated with the end groups, from anti-oxidant, or

from small amounts of impurities. They could result from all three sources. The

chemical shifts of minor components, including those from adjacent 1,2 polymeri-

zation units were not included in Table II.

III. Short Term Curing Characteristics

An attempt was made to monitor any chemical shift changes associated with the

initial curing reaction. A solution of HX-868 (BITA) curing agent in methylene

chloride was mixed with a sample of CTPB to which methylene chloride had been

added. The BITA was added far in excess of normal amounts. The carbon-13

spectrum was monitored for several hours, but no significant chemical shift

change was noted in the spectrum except for the appearance of two methylene

chloride peaks, a rather unusual phenomenon. Upon retrieving the sample from

the probe, it was found that the solution of BITA had separated from the solu-

tion of polymer, as if the two were not miscible. This did, however, explain

the presence of two methylene chloride resonances. The carbons near the end groups
                                      when curing occurs
must experience chemical shifts,/but their low intensities and unfavorable relax-

ation times make observation of them extremely difficult. Also the carbonyl of

the curing agent lies very close to that of the polymer, further increasing the

difficulty. As a result of these problems, the resonance lines associated with

end groups in the cured polymers was not observed.

A second type of aging reaction involving free radical attack on double

bonds of CTPB was investigated by adding a free radical initiator to a solution

of the polymer in dioxane. The free radical generating agent used was azo-bis-2,2-dimethylpropionitrile, which was added in weight percentage of 5.0% and curing was begun at 135°F, at which temperature the azo compound should have a half-life of at most several hours. To date only very small changes have been noted in the carbon-13 spectrum, but the lines have broadened noticeably, indicating that relaxation times have changed. It will be necessary to measure T_1's on this sample to determine if significant changes have occurred. The sample currently is being maintained at 135°F, and is monitored periodically.

Five samples of CTPB and dioxane were made up in the ratio of 0.82 g polymer to 1.5 ml dioxane. BITA (10%) was then added and the five samples were placed in heating blocks at 75, 95, 115, 135 and 150°F respectively. The cmr spectra were obtained periodically to see if changes could be detected in the cis-trans to vinyl ratio. The results are tabulated in Table III. The ratios were determined by dividing the sum of the intensities of the principal olefinic resonances (lines B_c and B_t) by those of the vinyl end group (lines K and L). The two examples were measured as a cross-check. Although there is considerable scatter in the data, there seems to be a trend toward decreasing cis-trans/vinyl proportions as curing proceeds. Although this is somewhat surprising, it may be an artifact as a result of increased linewidth of the backbone carbons due to relaxation effects as cross linking occurs. The vinyls should be much less affected by curing processes not involving them directly.

IV. Relaxation Properties of Cured Propellant Binder

When the magnetic vector resulting from the Zeeman effect on nuclear spins in a magnetic field is tipped away from its equilibrium position, it tends to return to equilibrium by relaxation processes, characterized by time constants called T_1's. In large molecules not possessing quadrupolar nuclei, the principal

relaxation mode is generally by means of nuclear dipolar coupling to the lattice. The efficiency of this nuclear-lattice coupling, and hence T_1, is governed by the motion of the nucleus, i.e., by the molecular tumbling rates. Any additional motions, such as segmental movement in polymers, modulates the relaxation processes. Thus, the measurement of T_1's provides an insight into the molecular motions, which should be directly relatable to the state of cure or aging in polymeric materials.

The relaxation times are measured by applying a 180 degree (π) pulse to the sample, waiting a time τ, followed by an observing 90 degree ($\pi/2$) pulse for a series of τ's. The T_1 of a given carbon is simply determined by the methods of first-order kinetics, i.e., the logarithm of residual resonance line intensity is plotted versus time (τ) and the slope of the resulting linear plot determines the relaxation parameter (T_1). Accuracy is typically 10 to 20%, although precision may be much higher for a given sample.

Samples of propellant binder which had been cured for 26 weeks at five temperatures (75, 95, 115, 135, and 150°F) were supplied by Thiokol Chemical Corp. In order to minimize the effects of uncontrolled variables, all samples were handled as similarly as possible; 0.82 g of binder was mixed with 1.5 ml of dioxane and the probe temperature was adjusted to 36°C for each run. Despite these precautions, the quality of the resulting data varied substantially. Also, even though magnet homogeneity was optimized before each run, resolution varied between samples. For these reasons the number data points available, F test of variance, and multiple correlation coefficient resulting from the least squares, linear regression fit have been included in the tables of T_1 results, so that the relative quality of the various numbers would be evident. The T_1 values measured for uncured CTPB and for the various cure temperatures are presented in Tables IV through IX. Table X contains a summary of the T_1 results.

Focusing attention on Table X, several things may be noted. First, for carbons having similar motional characteristics, the carbons with two attached protons should relax at twice the rate of carbons having a single carbon-hydrogen bond. This is noted to be qualitatively true in comparing carbons such as K and L or F and G. Also rotation about the G - L bond would tend to lengthen the T_1's of carbons K and L. Slightly larger T_1 values for K and L indicate there is some free rotation of the vinyl group. As segmental motion decreases, the T_1 values should decrease if the motion is such as to meet the motional narrowing criterion. Line widths indicate that the molecule is in the motional narrowing region, but this premise should be checked by measuring the nuclear overhauser effects in the samples. Although there is considerable scatter in the data, a trend seems to exist toward shorter T_1's as the samples are cured at higher temperatures, indicating that the motion of the chains is more restricted with aging as a result of cross linking. The effect is not dramatic, however, which probably indicates that segmental motion rather than molecular tumbling is the principal mode for coupling to the lattice. Segmental motion would likely not be greatly affected by chain extension, while molecular tumbling should be slowed substantially when chain length is effectively doubled by cross linking.

The T_1 values of the uncured polymer do not seem to fit at their logical place at one end of the range; this probably reflects the fact that it does not have curing agent in it, nor has it been in contact with plasticizer, aluminum powder, and ammonium perchlorate that are present in the normal propellant.

A check was made to see if solvent volume was a critical factor in measuring the T_1"s; the results are contained in Tables XI and XII. Solvent volume did not seem to be critical, so that if some solvent were lost by evaporation through the sample tube cap, it would not have produced the scatter noted in Table X, at least if mixing of the various samples was the same. Table XIII is the result

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of a T_1 measurement in a different solvent, methylene chloride, and T_1's measured therein are seen to be considerably shortened over those measured in dioxane.
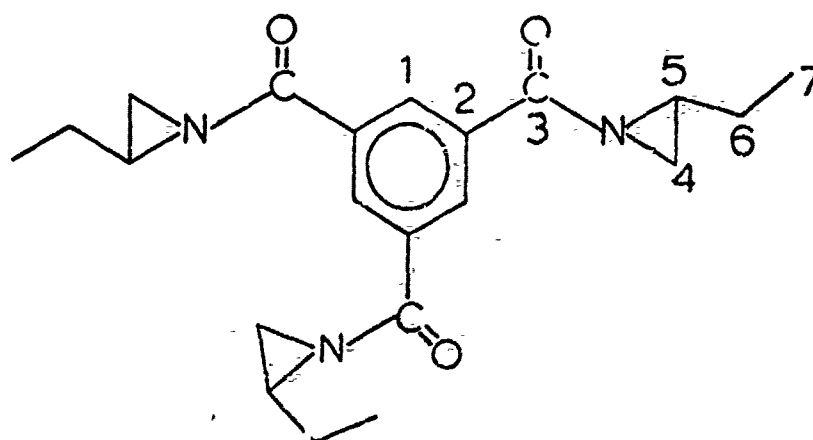
Figure 1. Numbering scheme for HX-868 (BITA) curing agent.
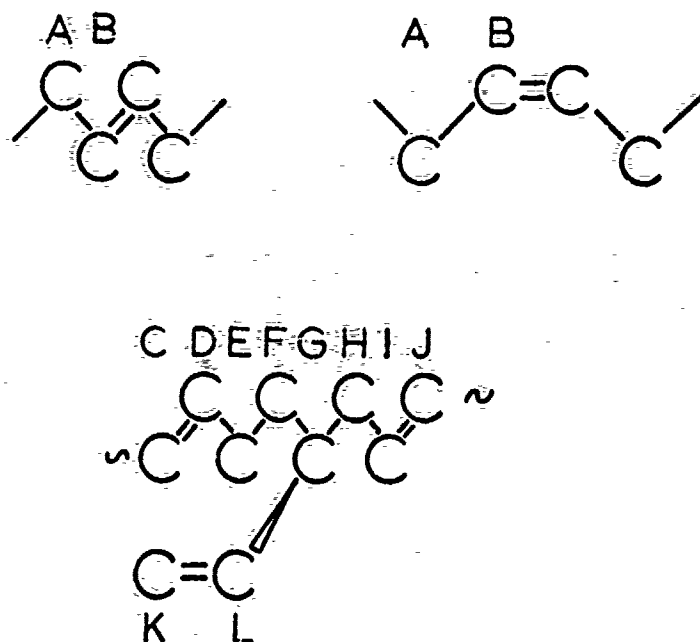
Figure 2. Identification scheme for polybutadiene polymer. _Cis_ and _trans_ carbons are identified by an appropriate subscript.

Table I. Carbon-13 Chemical Shifts of HX-868 (BITA)

Chemical Shift[a]	Assignment[b]
132.8	1
134.3	2
177.0	3
31.2	4
40.1	5
25.3	6
10.3	7
176.9	impurity
128.5	impurity

[a] In ppm relative to internal TMS

[b] See Fig. 1 for the numbering scheme.

Table II. Carbon-13 Chemical Shifts[b] of Carboxyl Terminated Polybutadiene

Carbon[a]	Chemical Shift[b]	
	Relative to Dioxane	Relative to TMS
A_c	- 39.4	27.8
A_t	- 34.1	33.1
B_c	62.5	129.7
B_t	63.1	130.3
C_c	62.6	129.8
C_t	63.2	130.4
D_c	63.0	130.2
D_t	63.5	130.7
E_c	- 41.9	25.3
E_t	- 36.7	30.5
F	- 32.7	34.5
G	- 23.3	43.9
H_t	- 28.6	38.6
I_c	60.9	128.1
I_t	61.4	128.6
J_c	64.7	131.9
J_t	64.4	131.6
K	47.4	114.6
L	75.7	142.9
CO_2H	111.5	178.7

[a]See Fig. 2 for assignment scheme.

[b]In ppm. Internal dioxane was used as a reference; the chemical shifts were converted to TMS scale using $\delta(TMS) - \delta(dioxane) = 67.2$ ppm.

Table III. The Ratio of Cis and Trans Carbon Resonances to Vinyl Carbon Resonances[a] in Rocket Propellant (CTPB) Cured at Various Temperatures.

Cure Temperature (°F)	Cure Time (days)	K[b]	L[c]
75	1	5.57	4.09
	4	5.86	4.81
	9	6.02	4.21
	22	5.61	3.85
95	1	5.53	4.09
	4	6.28	5.20
	9	5.20	4.25
	23	5.65	4.24
115	1	5.91	4.50
	4	5.94	5.14
	9	5.56	4.15
	22	5.53	3.82
135	2 hr	6.14	5.01
	4 hr	6.04	4.77
	8.5 hr	6.13	5.01
	18.5 hr	5.96	4.88
	2	6.04	5.10
	7	6.14	5.44
	12	5.54	3.97
	25	5.57	3.94
150	0	6.45	5.84
	2 hr	6.23	4.79
	4 hr	6.03	4.83
	8.5 hr	6.05	5.19
	19 hr	6.31	5.02
	3	5.85	4.91
	7	5.33	4.08
	12	5.19	3.94
	25	5.65	.27

[a]As determined carbon-13 magnetic resonance.

[b]The ratio of line intensities (B_c+B_t) to that of line K. See Fig. 2.

[c]The ratio of line intensities (B_c+B_t) to that of line L. See Fig. 2.

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Table IV. Carbon-13[a] Spin Lattice Relaxation Times (T_1) and Statistical Parameters for Uncured (CTPB) Propellant Binder[b]

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.63	10	8760	1.000
A_t	0.45	10	18,900	1.000
B_c	0.72	10	19	0.840
B_t	0.79	10	48	0.925
C_c	0.66	10	31	0.890
C_t	0.91	10	26	0.876
D_c	0.53	10	69	0.946
D_t	0.45	10	80	0.953
E_c	0.31	9	424	0.992
E_t	0.25	9	787	0.996
F	0.27	9	234	0.985
G	0.50	10	352	0.989
H_t	0.21	9	108	0.969
I_c	0.89	10	20	0.846
I_t	0.67	10	45	0.921
J_t	0.48	10	116	0.967
K	0.30	10	604	0.993
L	0.84	10	71	0.948

[a]Refer to Fig. 2 for assignment of the carbons as labeled in the left hand column.

[b]The sample was prepared with 0.8 g of polymer in 1.5 ml dioxane.

Table V. Carbon-13[a] Spin Lattice Relaxation Times (T_1) and Statistical Parameters for (CTPB) Propellant Binder[b] Cured 26 Weeks at 75°F.

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.65	10	3790	1.000
A_t	0.46	10	3160	0.999
B_c	0.83	10	97	0.961
F_t	0.83	10	207	0.981
C_c	0.95	10	96	0.961
C_t	1.03	10	76	0.951
D_c	0.57	4	693	0.999
D_t	0.74	10	263	0.985
E_c	0.30	7	43	0.946
E_t	0.27	8	168	0.983
F	0.34	8	756	0.996
G	0.51	10	426	0.991
H_t	0.32	8	219	0.987
I_c	0.59	10	87	0.957
J_t	0.56	10	390	0.990
K	0.44	10	180	0.979
L	0.91	10	98	0.961

[a]See footnote a, Table IV

[b]See footnote b, Table IV

Table VI. Carbon-13^a Spin Lattice Relaxation Times (T_1) and Statistical Parameters for (CTPB) Propellant Binder^b Cured 26 Weeks at 95°F.

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.66	10	3490	0.999
A_t	0.47	10	2810	0.999
B_c	0.84	10	208	0.981
B_t	0.82	10	117	0.968
C_c	0.93	10	178	0.978
C_t	0.97	9	119	0.972
D_c	0.70	10	173	0.978
D_t	0.60	10	335	0.988
E_c	0.41	9	37	0.918
E_t	0.25	8	392	0.992
F	0.36	8	97	0.971
G	0.54	10	369	0.989
H_t	0.27	8	220	0.987
I_c	0.52	9	96	0.966
I_t	0.76	10	149	0.974
J_t	0.82	10	209	0.981
K	0.46	10	535	0.993
L	0.88	10	49	0.927

^{a}See footnote a, Table IV

^{b}See footnote b, Table IV

Table VII. Carbon-13[a] Spin Lattice Relaxation Times (T_1) and Statistical Parameters for (CTPB) Propellant Binder[b] Cured 26 Weeks at 115°F.

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_t	0.46	10	8420	1.000
A_c	0.59	10	11,400	1.000
B_c	0.79	10	371	0.989
B_t	0.79	10	1510	0.997
C_c	0.85	10	2310	0.998
D_t	0.58	10	658	0.994
E_c	0.33	8	698	0.996
E_t	0.27	8	680	0.996
F	0.32	9	1520	0.998
G	0.49	10	1510	0.997
H_t	0.27	8	456	0.994
I_c	0.66	10	148	0.974
J_t	0.49	10	526	0.993
K	0.33	9	832	0.996
L	0.93	10	1170	0.995

[a]See footnote a, Table IV

[b]See footnote b, Table IV

Table VIII. Carbon-13[a] Spin Lattice Relaxation Times (T_1) and Statistical Parameters for (CTPB) Propellant Binder[b] Cured 26 Weeks at 135°F

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.68	10	1920	0.998
A_t	0.48	10	3880	0.999
B_c	0.79	10	148	0.974
B_t	0.87	10	290	0.987
C_c	0.80	10	52	0.931
C_t	1.04	10	137	0.972
D_c	0.76	9	111	0.970
D_t	0.52	8	48	0.943
E_c	0.30	4	75	0.987
E_t	0.27	7	155	0.984
F	0.45	7	19	0.888
G	0.66	9	89	0.963
H_t	0.26	7	42	0.945
I_t	0.87	8	27	0.904
J_t	0.68	8	72	0.961
K	0.39	8	203	0.986
L	1.15	10	157	0.975

[a]See footnote a, Table IV

[b]See footnote b, Table IV

Table IX. Carbon-13[a] Spin Lattice Relaxation Times (T_1) and Statistical Parameters for (CTPB) Propellant Binder[b] Cured 26 Weeks at 150°

Carbon	T_1 (sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.56	10	8710	1.000
A_t	0.44	10	2720	0.999
B_c	0.69	10	1550	0.997
B_t	0.76	10	3950	0.999
C_c	0.82	10	637	0.994
D_t	0.57	10	534	0.993
E_c	0.31	7	244	0.990
E_t	0.24	7	158	0.985
F	0.30	7	385	0.994
G	0.39	9	951	0.996
H_t	0.25	7	555	0.996
I_c	0.46	7	52	0.955
J_t	0.58	8	866	0.997
K	0.36	8	639	0.995
L	0.84	10	424	0.991

[a] See footnote a, Table IV

[b] See footnote b, Table IV

Table X. Summary of Carbon-13 Relaxation Times (T_1 in sec.) Measured on Rocket Propellant Binder[a] (CTPB) Cured for 26 Weeks at Various Temperatures

			Cure Temperature			
Carbon[b]	uncured	75°F	95°F	115°F	135°F	150°F
A_c	0.63	0.65	0.66	0.60	0.68	0.56
A_t	0.45	0.46	0.47	0.46	0.48	0.44
B_c	0.72	0.83	0.84	0.79	0.79	0.69
B_t	0.79	0.83	0.82	0.79	0.87	0.76
C_c	0.58					
C_t	0.66	0.95	0.94	0.85	0.80	0.82
D_c	0.54	0.57	0.68		0.76	
D_t	0.45	0.74	0.60	0.58	0.52	0.57
E_c	0.31	0.30	0.41	0.33	0.30	0.31
E_t	0.25	0.27	0.25		0.27	0.25
F	0.27	0.34	0.37	0.32	0.45	0.30
G	0.50	0.51	0.54	0.49	0.66	0.39
H_t	0.21	0.32	0.27	0.27	0.26	0.25
I_c	0.89	0.59	0.52	0.66	0.87	0.46
I_t	0.67		0.76			
J_t	0.48	0.56	0.82	0.49	0.68	0.58
K	0.30	0.44	0.46	0.33	0.39	0.36
L	0.84	0.91	0.88	0.93	1.15	0.84

[a]Each sample consisted of 0.82 g binder mixed with 1.5 mℓ of dioxane

[b]See Fig. 2

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Table XI. Effect of Solvent Volume[a] on the Carbon-13[b] Relaxation Times (T_1) and Statistical Fit for (CTPB) Propellant Binder Cured 26 Weeks at $135°F$

Carbon	T_1 (sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.65	11	2630	0.998
A_t	0.56	11	2960	0.999
B_c	0.85	11	1320	0.997
B_t	0.86	11	3590	0.999
D_t	0.72	10	592	0.993
E_c	0.53	6	37	0.950
E_t	0.35	6	330	0.994
F	0.38	6	147	0.987
G	0.61	9	256	0.987
H_t	0.29	4	59	0.984
I_t	0.85	10	247	0.984
J_t	0.69	10	305	0.987
K	0.46	9	191	0.982
L	1.38	11	320	0.986

[a] The sample was prepared with 0.82 g of polymer in 3.0 ml dioxane. Compare Table VIII.

[b] See footnote a, Table IV

Table XII. Effect of Solvent Volume[a] on the Carbon-13[b] Relaxation Times (T_1) and Statistical Fit for (CTPB) Propellant Binder Cured 26 Weeks at 150°F.

Carbon	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.59	7	16,900	1.000
A_t	0.50	6	10,820	1.000
B_c	0.90	7	2170	0.999
B_t	0.95	6	7400	1.000
C_c	0.97	7	950	0.997
C_t	1.11	7	695	0.996
D_t	0.58	4	249	0.996
E_c	0.47	3	189	0.997
E_t	0.31	3	473	0.999
F	0.37	3	574	0.999
G	0.62	6	3723	0.999
H_t	0.30	3	1622	1.000
I_t	0.69	5	1041	0.999
J_c	0.42	3	357	0.999
J_t	0.70	5	137	0.989
K	0.41	5	298	0.995
L	1.07	7	478	0.995

[a] The sample was prepared with 0.82 g polymer in 3.0 mℓ dioxane. Compare Table IX.

[b] See footnote a, Table IV

Table XIII. The Effect of Solvent Change on Relaxation Times (T_1) and Statistical Fit for Uncured CTPB.[a] Methylene Chloride as Solvent.

Carbon[b]	T_1(sec)	No. of Data Points	F Test of Variance	Correlation Coefficient (R)
A_c	0.39	12	2540	1.00
A_t	0.30	12	3080	1.00
B_c	0.43	10	540	0.993
B_t	0.50	9	546	0.994
C_c	0.47	9	1020	0.997
E_c	0.25	11	575	0.99
E_t	0.20	11	1920	1.00
F	0.30	12	145	0.97
G	0.32	12	8930	1.00
H_t	0.16	10	1700	1.00
I_c	0.38	10	228	0.983
I_t	0.43	9	408	0.992
J_c	0.33	9	208	0.984
J_t	0.35	8	557	0.995
K	0.21	9	763	0.995
L	0.51	8	764	0.996

[a]The sample was prepared with CH_2Cl_2 (20%) added to uncured CTPB. Compare Table IV.

[b]See footnote a, Table IV.